Chapter 19

A dictionary of terms and expressions

D.S.J. Jones and P.R. Pujadó

A

Abel flash points

This is a test procedure for determining the flash point of light distillate such as kerosene. The flash points determined by this method will be in the range of 85–120°C. The apparatus consists of a water bath with a heating source into which is suspended a cup containing the material to be tested. The water bath is heated and retained at a fixed temperature. The temperature of the sample being tested in the cup is measured by a thermometer. The lid of the cup contains a shutter and a small gas burner from which a flame of determined length exits. The rate of temperature rise of the test material is noted and at predetermined temperatures the shutter is opened and the burner flame exposed to the space above the test liquid in the cup. The temperature at which a flame is observed crossing the surface of the oil sample when the burner is dipped into the cup is the flash point. The ASTM name and number for this test is D56-01 Standard Test Method for Flash Point by Tag Closed Tester.

Absorption units

Absorption units usually consist of a trayed or packed tower in which a gas stream is contacted with a lean solvent in a counter current flow. Usually the gas stream enters below the bottom tray or packed bed and rises up the tower meeting the solvent liquid stream which enters the tower above the top tray or packed bed flowing down the tower. Undesirable material in the gas stream is selectively absorbed into the liquid stream. This liquid stream then enters a stripping column (usually a Steam Stripper), where the absorbed material is stripped off and leaves as an overhead product. The stripped solvent stream is then rerouted to the absorber tower to complete the cycle. These processes are used in petroleum refining to remove heavy hydrocarbons from a light

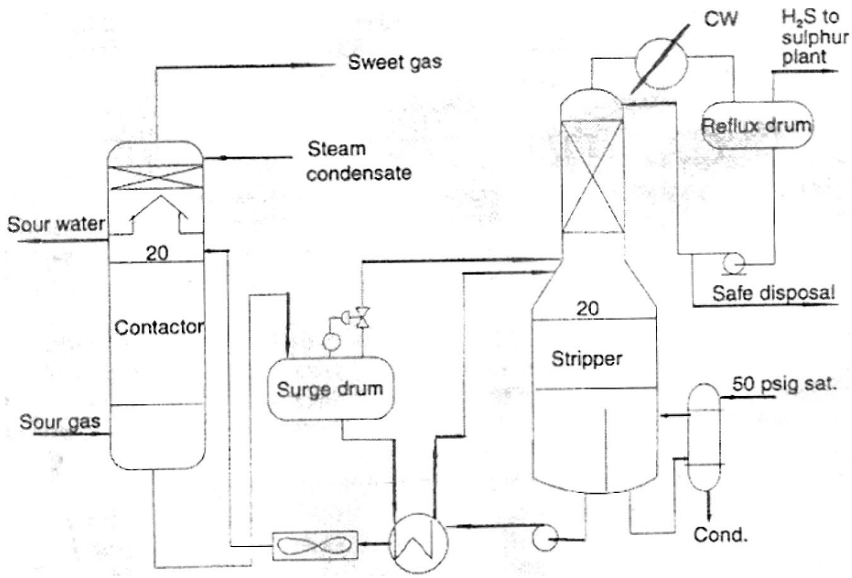


Figure 19.A.1. A schematic of a typical absorption unit.

gas stream. More commonly this type of unit is used in gas treating for the removal of H_2S from a gas stream (see Chapter 10 of this book). A schematic flowsheet of an absorption (gas treating unit) is shown as Figure 19.A.1.

Anhydrous hydro fluoric acid

Anhydrous hydrofluoric acid (AHF) is a colorless, mobile liquid that boils at 67°F at atmospheric pressure, and therefore requires pressure containers. The acid is also hygroscopic therefore its vapor combines with the moisture of air to form "fumes". This tendency to fume provides users with a built-in detector of leaks in AHF storage and transfer equipment. On the other hand, care is needed to avoid accidental spillage of water into tanks containing AHF. Dilution is accompanied by a high release of heat. Hydrofluoric acid is very corrosive. It attacks glass, concrete, and some metals—especially cast iron and alloys that contain silica (e.g., Bessemer steels). The acid also attacks such organic materials such as leather, natural rubber, and wood, but does not promote their combustion (see Chapter 15 for details).

Air condensers and coolers

Air cooling of process streams or condensing of process vapors is more widely used in the process industry than cooling or condensing by exchange with cooling water. The

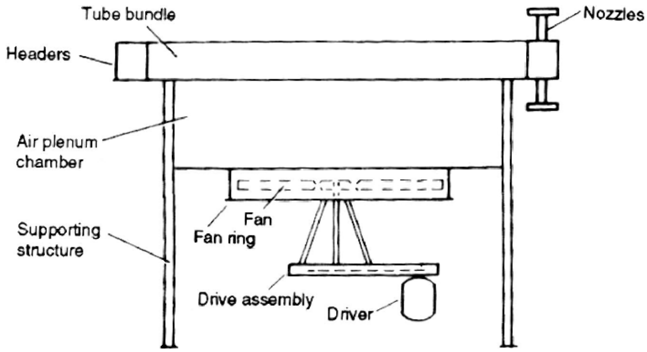


Figure 19.A.2. A forced air flow arrangement.

use of individual air coolers for process streams using modern design techniques has economized in plant area required. It has also made obsolete those large cooling towers and ponds associated with product cooling. This item in Chapter 18 describes air coolers in general and outlines a method to estimate surface area, motor horsepower, and plant area required by the unit.

As in the case for shell and tube exchangers there are many excellent computer programs that can be used for the design of air coolers. The method given in Chapter 18 for such calculation may be used in the absence of a computer program or for a good estimate of a unit. The method also emphasizes the importance of the data supplied to manufacturers for the correct specification of the units.

Figures 19.A.2 and 19.A.3 show the two types of air coolers used in the process industry. Both units consist of a bank of tubes through which the fluid to be cooled or condensed flows. Air is passed around the tubes either by a fan located below the tubes

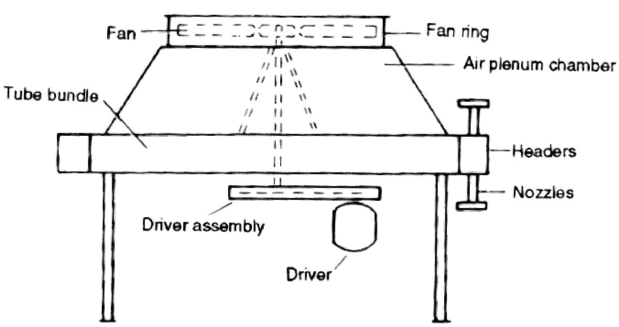


Figure 19.A.3. An induced air flow arrangement.

(Figure 19.A.2) forcing air through the tube bank or a fan located above the tube bank drawing air through the tube bank (Figure 19.A.3). The first arrangement is called 'Forced draft' and the second 'Induced draft'.

Air in both cases is motivated by a fan or fans driven by an electric motor or a steam turbine or in some cases a gas turbine. The fan and prime driver are normally connected by a 'V' belt or by a shaft and gear box. Electric motor drives are by far the most common prime drivers for air coolers.

The units may installed on a structure at grade or as is often the case on a structure above an elevated pipe rack. Most air coolers in condensing service are elevate above pipe racks to allow free flow of condensate into a receiving drum.

Air systems

All chemical and petroleum plants require a supply of compressed air to operate the plant and for plant maintenance. There are usually two separate systems and these are:

- Plant air system
- Instrument air system

Plant air is generally supplied by a simple compressor with an after cooler. Very often when plant air is required only for maintenance this is furnished by a mobile compressor connected to a distribution piping system. Air for catalyst regeneration and the like is normally supplied by the regular gas compressor on the unit. Instrument air should always be a separate supply system. Compressed air for instrument operation must be free of oil and dry for the proper function of the instruments it supplies. This is a requirement which is not necessary for most plant air usage. A reliable source of clean dry instrument air is an essential requirement for plant operation. Failure of this system means a complete shut down of the plant.

Figure 13.36 in Chapter 13 of this Handbook shows a typical instrument air supply system. Atmospheric air is introduced into the suction of one of two compressors via an air filter. The compressors are usually reciprocating or screw type non-lubricating. Centrifugal type compressors have been used for this service when the demand for instrument air is very high. The air compressors discharge the air at the required pressure (usually above 45 psig) into an air cooler before the air enters one of two dryers. One of the compressors is in operation while the other is on standby. The operating compressor is usually motor driven with a discharge pressure operated on/off start up switch. The standby compressor is turbine (or diesel engine) driven with an automatic start up on low/low discharge pressure switch.

The cooled compressed air leaves the cooler to enter the dryers. There are two dryer vessels each containing a bed of desiccant material. This material is either silica gel (the most common), alumina, or in special cases zeolite (molecular sieve). One of the two dryers is in operation with the compressed air flowing through it to be dried and to enter the instrument air receiver. The desiccant in the other dryer is being simultaneously regenerated. Regeneration of the desiccant bed is effected by passing through the bed a stream of heated air and venting the stream to atmosphere. This heated stream removes the water from the desiccant to restore its hygroscopic properties. At the end of this heating cycle cooled air is reintroduced to cool down the bed to its operating temperature. When cool, the unit is then shut in ready to be switched into operation for the first dryer to start its regeneration cycle. The various operating and regeneration phases are automatically obtained by a series of solenoid valves operated by a sequence timer switch control. These dryers (often including the compressor and receiver items) are packaged units supplied, skid mounted, and ready for operation.

The instrument air receiver vessel is a pressure vessel containing a crinkled wire mesh screen (CWMS) before the outlet nozzle. It is high-pressure protected by a pressure control valve venting to atmosphere, and of course is also protected by a pressure safety valve. The air leaves the top of this vessel to enter the instrument air distribution system servicing all the plants in the complex.

Alkylation

Alkylation as utilized in the petroleum industry was developed independently by UOP, Shell, the Anglo Iranian Company, and Texaco in 1932–1936. Motor fuel alkylation in the petroleum refining industry refers to the acid catalyzed conversion of C_3–C_5 olefins with isobutane into highly branched C_5–C_{12} isoparaffins collectively called alkylate, a valuable gasoline blending component. A major constituent of alkylate is 2,2,4-trimethyl pentane which is defined as 100 on the octane scale.

Alkylation reactions are catalyzed by liquid and solid acids, including H_2SO_4, $AlCl_3$–HCl, HF, HF–BF_3, H_2SO_4–HSO_3F (fluorosulfuric acid), trifluoromethane sulfonic acid chlorided Pt alumina, BF_3 on alumina, zeolites, and ion exchange resins. However, the catalysts and associated processes commercialized during World War II for aviation gasoline, were HF alkylation and sulfuric acid alkylation. These are the process met with in most of today's refineries (see Chapter 9 for a fuller historical description).

The chemistry of the alkylation process is quite complex and is given in some detail in Chapter 9 of this Handbook. Briefly it can be summarized by the following reaction stages:

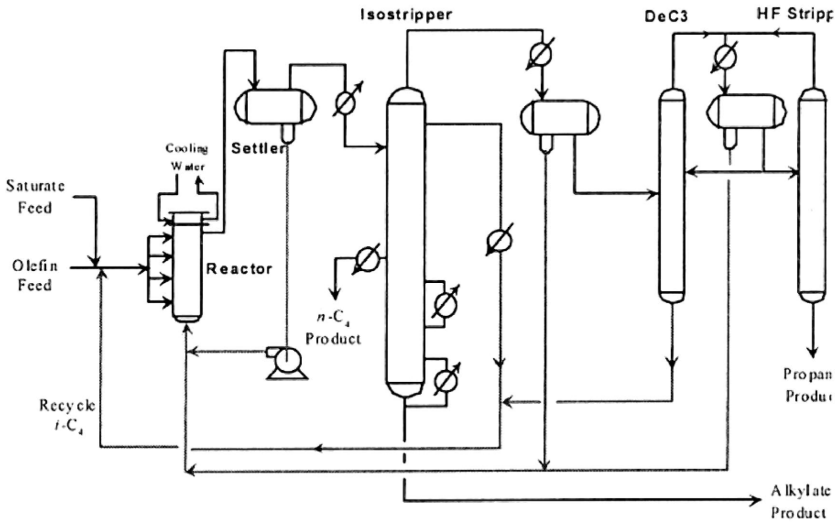


Figure 19.A.4. AHF alkylation process.

- Initiation $C_4 = + HF \text{ (or } H_2SO_4) \rightarrow C_4^{+} + F^{-}$
- Alkylation $C_4^{+} + C_4 \rightarrow C_8^{+}$
- Saturation and Continuation $C_8^{+} + iC_4 \rightarrow C_8 + iC_4^{+}$
- Polymerization $C_8^{+} + C_4 = \rightarrow C_{12}^{+}$
- Cracking $C_{12}^{+} \rightarrow iC_5^{+} + C_7$

The last two reactions explain the variety of side products occurring typically at either end of the boiling range of primary product.

Alkylation unit HF

Figure 19.A.4 is a simplified process flow diagram for the UOP propylene–butene HF alkylation process.

After pretreatment to remove H_2S and mercaptans the olefin feeds are combined with a large excess of recycle isobutane. This mixture provides an 6–14 isobutane/olefin molar ratio which is fed with a circulating HF acid catalyst to the shell side of a water-cooled reactor. The alkylation reaction is very fast with 100% olefin conversion. The excess isobutane, alkylate product, non-reactive hydrocarbons (propane, n-butane) in the feeds and the acid catalyst pass on to the settler vessel. The dense acid phase

separates from the hydrocarbons rapidly by gravity and is then pumped back to the reactor. The hydrocarbons containing dissolved HF flow off the top of the settler to the isostripper. This is a large tower with two sidedraws. Its primary function is to produce the recycling isobutane stream to maintain the high isobutane/olefin molar ratio of the reactor feed. The tower typically has two reboilers. Alkylate is drawn off the bottom of the tower, cooled in exchangers, and sent to product storage. The next product draw up the tower is the n-butane sidedraw and above that is the isobutane recycle draw. The isostripper overhead vapor is a propane-enriched isobutane stream and HF which is condensed and separated in a settling drum. The HF phase is pumped back to the reactor section. The HF saturated hydrocarbon phase is charged to the depropanizer.

This tower and its associated HF stripper remove propane from the isobutane recycle. The depropanizer bottoms is returned to the reactors as part of the recycle isobutane. The depropanizer overhead containing the propane product and HF are condensed and separated in the overhead receiver. The acid phase is returned to the reactor section and the acid-saturated propane is stripped free of acid in the HF Stripper column. The HF stripper bottoms is an acid-free propane product which is treated with hot alumina to remove organic fluorides, cooled and treated with KOH pellets to remove traces of HF and water.

The UOP HF Alkylation process contains an acid regenerator. This unit takes a small sidestream of the recycle HF and strips out the acid leaving the hydrocarbon to join the isobutane recycle. (A full process description and discussion is given in Chapter 9.)

Alkylation unit H_2SO_4

Figure 19.A.5 is a simplified process drawing of a H_2SO_4 alkylation unit. Today there are two processes for H_2SO_4 alkylation, the cascade process licensed by Exxon Mobil and MWKellogg and the Stratco effluent refrigerated process. The one shown as Figure 19.A.5 is the cascade process. Full details of this process and the Stratco process are given in Chapter 14.

Amine solvents

Amines are used as solvents in the removal of hydrogen sulfide from refinery gas streams. There are many amine compounds used for this purpose. The more common of these are listed as follows

- Monoethanol amine (MEA)
- Diethanol amine (DEA)
- Diglycol amine (DGA)

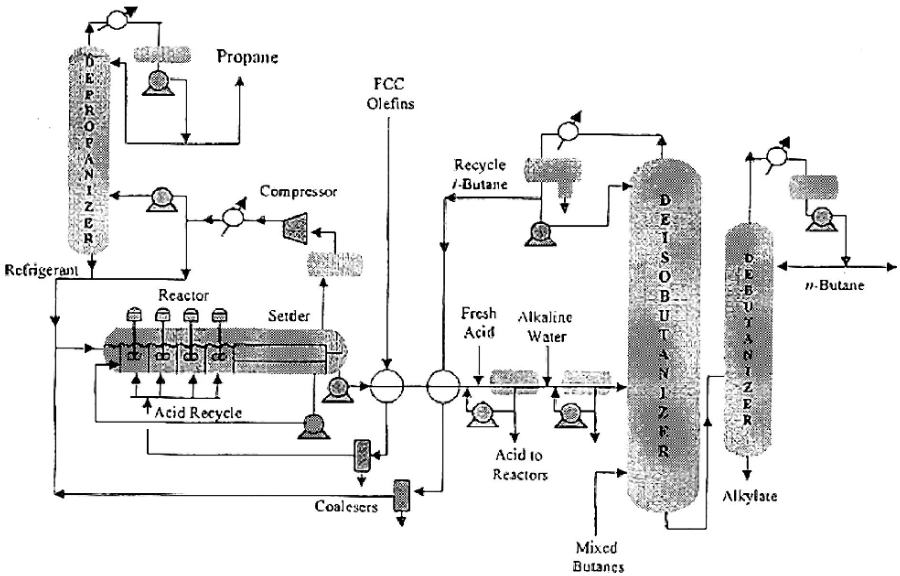


Figure 19.A.5. H_2SO_4 alkylation process.

There are also two proprietary processes licensed by Shell Petroleum which are used extensively world wide. These are the ADIP process and the Sulfinol process.

Monoethanol amine

MEA is the most basic (and thus reactive) of the ethanol amines. MEA will completely sweeten natural gases removing nearly all acid gases if desired. The process is well proven in refinery operations.

Like all of the amine solvents used for acid gas removal, MEA depends upon its amino nitrogen group to react with the acidic CO_2 and H_2S in performing its absorption. MEA is considered a chemically stable compound. If there are no other chemicals present it will not suffer degradation or decomposition at temperatures up to its normal boiling point.

The process reactions are given below.

$$HOCH_2CH_2NH_2 = RNH_2$$
$$2RNH_2 + H_2S \rightarrow (RNH_3)_2S$$
$$(RNH_3)_2S + H_2S \rightarrow 2RNH_3HS$$

Some of the degradation products formed in these systems are highly corrosive. They are usually removed by filtration or reclaimer operations. Filtration will remove corrosive byproducts such as iron sulfide. Reclaiming is designed to remove heat stable salts formed by the irreversible reaction of MEA with COS, CS_2 (Carbonyl Sulfide and Carbon Disulphide). The reclaimer operates on a sidestream of 1–3% of the total MEA circulation. It is operated as a stream stripping kettle to boil water and MEA overhead while retaining the higher boiling point heat stable salts. When the kettle liquids become saturated at a constant boiling point with the degradation products it is shut in and dumped to the drain.

Diethanol amine

DEA does not degrade when contacted with CS_2, COS, and mercaptans as MEA does. Because of this, DEA has been developed as a preferred solvent when these chemicals are present in the stream to be treated.

DEA is a weaker base (less reactive) than MEA. This has allowed DEA to be circulated at about twice the solution strength of MEA without corrosion problems. DEA systems are commonly operated at strengths up to 30 wt% in water and it is not unusual to see them as high as 35 wt%. This results in the DEA solution circulation rate usually being a little less than MEA for the same system design parameters.

The process reactions are shown below.

$$
\begin{aligned}
HOCH_2CH_2NHCH_2CH_2OH &= R_2NH = DEA \\
2R_2NH + H_2S &\rightarrow (R_2NH_2)_2S \\
(R_2NH_2)_2S + H_2S &\rightarrow 2R_2NH_2HS
\end{aligned}
$$

Because the system has much fewer corrosion problems and removes acid gases to nearly pipeline specifications it has been installed as the predominant system in recent years.

Diglycol amine

This process uses 2-(2-amono ethoxy) ethanol at a recommended solution strength of 60 wt% in water. DGA has almost the same molecular weight as DEA and reacts mole for mole with acid gases. DGA seems to tie up acid gases more effectively so that the higher concentration of acid gas per gallon of solution does not cause corrosion problems as experienced with the usual amine processes.

Table 19.A.1. A summary of the common amines

Amine	MEA	DEA	DGA
Molecular weight	61.1	105.1	105.14
Boiling point °F	339	514	405
Freezing point °F	51	77	−9.5
Sg @ 77°F (25°C)	1.0113	1.0881	1.0572
Visc @ 77°F Cp	18.95	352	40
Visc @ 140°F Cp	5.03	53.9	6.8
Flash point °F	200	295	260

The system reactions are given below.

$$HOCH_2CH_2OCH_2CH_2NH_2 = RNH_2 = DGA$$

$$2RNH_2 + H_2S \rightarrow (RNH_3)_2S$$

$$(RNH_3)_2S + H_2S \rightarrow 2RNH_3HS$$

DGA does react with COS and mercaptans similarly to MEA but forms bis (hydroxy, ethoxy ethyl) urea, BHEEU. BHEEU can only be detected using an infra-red test rather than chromatography. Normal operating levels of 2–4% BHEEU are carried in the DGA without corrosion problems. BHEEU is removed by the use of a reclaimer identical to that for an MEA system but operating at 385°F (196°C). Materials of construction are the same as those for MEA systems.

DGA allows H_2S removal to less than 1/4 grain per 100 Scf (about 0.006 kg per 1,000 cubic meters) and removes CO_2 to levels of about 200 ppm using normal absorber design parameters.

A summary of these amines is given in Table 19.A.1.

Amine units

The use of chemically "basic" liquids to react with the acidic gases was developed in 1930. The chemical used initially was tri-ethanolamine (TEA). However as mono-ethanolamine (MEA) became commercially more available it became the preferred liquid reactant due to its high acid gas absorptivity on a unit basis.

Since 1955, numerous alternative processes to MEA have been developed. These have fewer corrosion problems and are to a large extent more energy efficient. Inhibitor systems have however been developed which have eliminated much of the MEA corrosion problems. Some of these newer processes also are designed to selectively remove the H_2S, leaving the CO_2 to remain in the gas stream.

A process diagram of a typical amine gas treating unit is given in Chapter 10 in of this Handbook and is shown as Figure 19.A.1. A brief description of such a unit is as follows:

Referring to the above flow sheet, sour gas (rich in H_2S) enters the bottom of the trayed absorber (or contactor). Lean amine is introduced at the top tray of the absorber section to move down the column. Contact between the gas and amine liquid on the trays results in the H_2S in the gas being absorbed into the amine. The sweet gas is water washed to remove any entrained amine before leaving the top of the contactor.

Rich amine leaves the bottom of the contactor to enter a surge drum. If the contactor pressure is high enough, a flash stream of H_2S can be routed from the drum to a trayed stripper. The liquid from the drum is preheated before entering a 20 tray stripping column on the top tray. This stripper is re-boiled with 50 psig saturated steam. High temperatures cause amines to break down. The H_2S is stripped off and leaves the reflux drum usually to a sulfur production plant. Sulfur is produced in this plant by burning H_2S with a controlled air stream, and then reacting H_2S with SO_2 over a catalyst.

The lean amine leaves the stripper and is cooled. The cooled stream is routed to the contactor.

Amine absorber

Amine absorbers do not have a high-tray efficiency. Generally, the efficiency of a contactor will range between 10% and 20%. This can be determined on an operating plant using plant data to determine the number of theoretical trays required to achieve the plant's operating performance. There are several accepted methods to calculate theoretical trays in this service. Among these are the MCabe Thiele graphical Method and the calculation method described by the following equation. This later calculation method is considered by many to be the sounder and more accurate of the methods available. The equation used for determining the theoretical trays for the absorption process is as follows:

$$N = \left[\frac{\text{Log } 1/q\,(A-1)}{\text{Log } A}\right] - 1$$

where

N = Number of theoretical trays.

$q = \dfrac{\text{Moles } H_2S \text{ in Lean gas}}{\text{Moles } H_2S \text{ in Feed gas}}$

A = Absorption Factor LK/V

The absorption factor is obtained from the equation:

$$A = \frac{a(1 + R - r)(1 - q)}{pp/P}$$

where

A = The absorption factor.
a = Mole fraction of H_2S in gas feed.
R = Moles MEA/moles H_2S absorbed.
r = Residual H_2S in lean MEA solution.
pp = Partial pressure of H_2S in rich amine solution.
P = Tower pressure psia.

Note: The above equations are suitable for all absorbents.

The Tower: The conventional Amine Contactor is divided into two parts:

The Absorption Section
The Water wash section

This is shown in Figure 19.A.6.

The lean amine enters the tower above the top absorber tray, through a distributor. It flows down the absorber section trays counter current to the rich gas moving up the tower. The rich gas enters the tower via a distributor under the bottom absorber tray. The H_2S contained in the gas is absorbed by the amine solvent by mass transfer on the trays. The rich amine leaves the bottom of the tower to the amine stripper column. The lean gas leaves the top of the of the absorber section to enter the water wash section of the tower. This wash section contains about 4–5 trays or a packed bed. Water is introduced above the top wash tray and flows down counter current to the lean gas to remove any entrained amine in the gas. The water is collected in a chimney tray and pumped to the oily water sewer. The washed gas leaves the top of the tower into the gas system.

Anhydrous ammonia

Ammonia is used in the refinery to neutralize vapor containing HCL at the overhead section of the atmospheric crude distillation tower. The ammonia is injected into the vapor spaces above the top four (or five) trays of the tower and into the overhead vapor line. The ammonia may be in the anhydrous form and introduced directly from cylinders or may be in the form of an aqueous solution. The aqueous form is injected from a storage bullet by means of metering pumps.

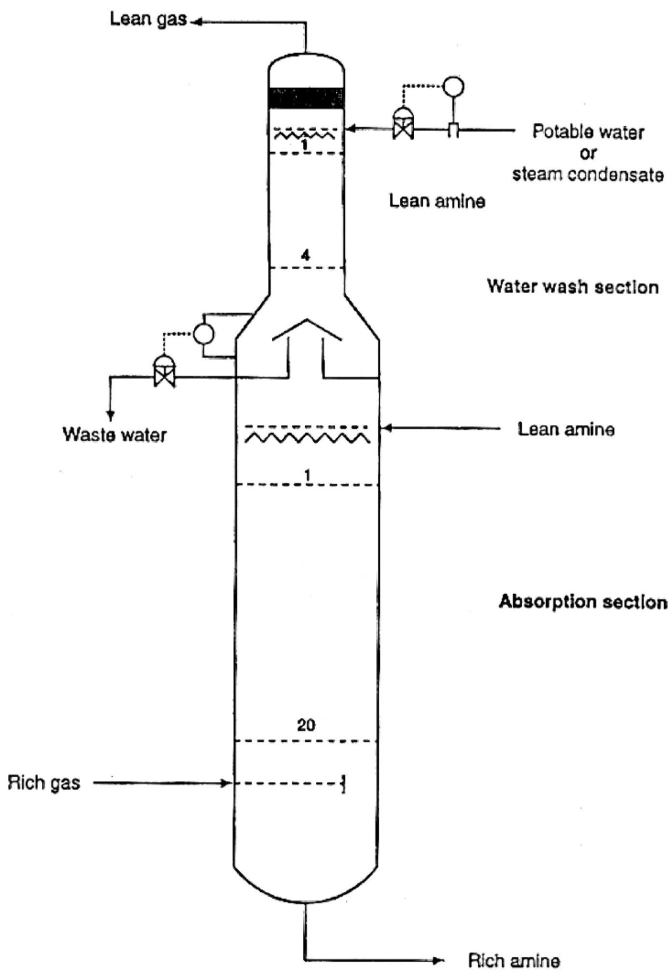


Figure 19.A.6. A typical amine absorber for MEA or DEA unit.

API codes

API stands for the American Petroleum Institute. The purpose of this body is to provide the industry with a set of standards which defines the design and measurement parameters that will be used in the petroleum industry. These codes cover such items as: vessel design, oily water separators, boiler design, safety items etc, and a number of laboratory test procedures for feed and petroleum products.

API gravity

This item is used in the compilation of most crude assays (see Chapter 1 of this Handbook). Although not a laboratory test as such it is derived from the standard test to determine the specific gravity of a liquid. The correlation between specific gravity and degrees API is as follows:

$$\text{Sp Gr} = \frac{141.5}{131.5 + {}^{\circ}\text{API}}$$

The specific gravity and the API are at 60°F. Note API is always quoted in degrees.

Aromatics

Aromatics are present throughout the entire boiling range of crude oil above the boiling point of benzene, the compound with the lowest boiling point in the homologue. These compounds consist of one or more closed conjugated rings with one or more alkyl groups attached. The lighter aromatics such as benzene, toluene, and the xylenes are removed as products in the petroleum chemical plants (see Chapter 12 of this Handbook). In the energy petroleum refinery these lighter aromatics are included in the finished gasoline products to enhance the octane rating of the products. Indeed the refinery process of catalytic reforming is aimed at converting the lower octane compounds (predominately naphthenes) into the high octane light aromatics. The heavier aromatic compounds however are often undesirable compounds in many products, such as kerosene, jet fuel, and many lube oils. In these cases the aromatic compounds are either converted (de-aromatizing hydrotreater for kerosenes) or removed by solvent extraction as in the case of lube oils.

The production of benzene, toluene, ethyl benzene, and the xylenes in the petrochemical refinery commences with the catalytic reforming of the naphtha product produced in the normal energy refinery. This reformate is treated to remove the residual aliphatic compounds of the naphtha by solvent extraction. The rich aromatic stream is then subjected to a series of distillation processes and selective con version to maximize the BTX products required. A typical configuration for an aromatic complex is shown in Figure 19.A.7.

This is one of many configurations for aromatic production. In Figure 19.A.7, the production maximizes benzene and ortho xylene at the expense of some toluene and all of ethyl benzene. This is accomplished by a cryogenic de-alkylation unit to produce more benzene, and a catalytic isomerization unit to convert ethyl benzene to ortho xylene.

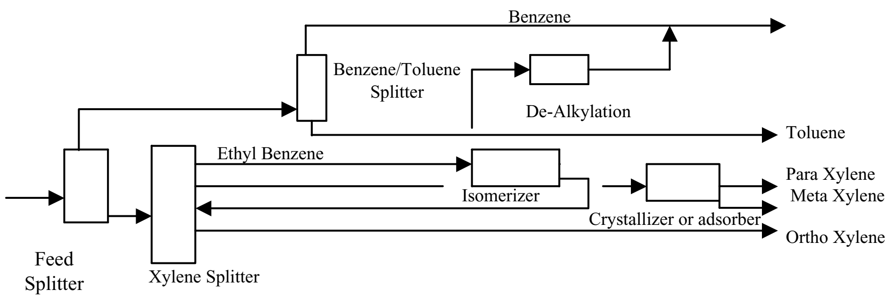


Figure 19.A.7. A typical aromatic plant configuration.

Ash content (Petroleum)

Petroleum ash content is the non-combustible residue of a lubricating or fuel oil determined in accordance with ASTM D582—also D874 (sulfated ash).

ASME (American Society of Mechanical Engineers)

The American Society of Mechanical Engineers has been a world leader in codes, standards, accreditation, and certification for over a century. These programs have now been extended to include the registration (certification) of quality systems in conformance with the standards set by the International Organization of Standardization (ISO). In the petroleum industry, this organization sets the quality requirements for vessel fabrication, piping and in particular the boiler code among many other standard definitions.

Asphalt

Asphalt is a group of products produced from the vacuum distillation residue of crude oil. The products that make up this group have distinct properties that must be met by the treating of the vacuum residue.

There are two major categories of asphalt products. These are:

- Paving and Liquid Asphalt
- Roofing Asphalt

The paving grades will have a penetration specification of 300 (30.0 mm) or less @ 77°F and 100 g weight, while the softer liquid grades will have a penetration of 300 and higher.

The liquid asphalt grades are typified as, RC (rapid curing), MC (medium curing), and SC (slow curing) each of these grades will also have 4 viscosity grades as given below:

70 grade—RC/MC/SC	70–140 Cs @ 140°F.
250 grade—RC/MC/SC	250–500 Cs
800 grade—RC/MC/SC	800–1,600 Cs
3,000 grade—RC/MC/SC	3,000–6,000 Cs.

Rapid curing cutbacks are penetration asphalt and naphtha blends having a viscosity range from 75 SSF @ 77°F to 600 SSF @ 180°F. The naphtha content may be as high as 75 vol%. Cutbacks are hot sprayed onto existing roads as a binding medium for new wearing surfaces.

Medium curing cutbacks are penetration grade asphalt and kerosene blends with four grades having the same viscosities as the RC cutbacks. These are used in road building in the same way as the RC cutbacks.

Slow curing cutbacks are penetration asphalt and gas oil blends normally produced directly from the crude oil atmospheric or vacuum distillation. The volume produced is small and they are used mainly as a gravel dust layer or mixed with aggregates for cold patching of asphalt surfaces.

Roofing asphalt

The second largest asphalt use is that for roofing. Most of these asphalts are produced by air blowing. There are three major roofing grades and may be classified by penetration and softening points. These are:

	Pen @ 77°F	Softening point °F
Type 1	25–50	140–150
Type 2	20–30	166–175
Type 3	15–25	190–205

Type 1 grade is used on ‘Dead Flat’ roof while the other two are used on intermediate and steep slope roofs, respectively.

Asphalt blowing process

Blowing air into a vessel containing asphalt from vacuum distillation or the de asphalting process will change its penetration and softening properties. Among the variables that affect the manufacture of air blown asphalt are:

- The rate of the air injected
- The temperature of the asphalt
- Retention time of the asphalt
- The system pressure

Description and details of this process are given in Chapter 12 in of this Handbook.

Asphaltenes

Asphalt is basically a colloidal dispersion of asphaltenes in oil with resins as the stabilizing agent. The quantities of these can vary widely with the type of crude.

Asphaltenes can be hydrogenated to resins, resins to oils. Resins can be oxidized to asphaltenes, oil to resins. Thus:

$$\begin{array}{lcl} \text{Asphaltenes} + H_2 \searrow & & H_2 \rightarrow \text{Oil} \\ & & + \\ & \text{Resins} & \\ & + & \\ & & \nwarrow \\ \text{Asphaltenes} + O_2 & & O_2 + \text{Oil} \end{array}$$

Oxidation is really a misnomer, as air blown asphalt has essentially the same oxygen content as the charge. Air blowing asphalt increases the asphaltene content, hardens it, decreases penetration, increases softening, and reduces ductility. Basically air blowing is a polymerization process following the route below:

1. Addition of O_2 to form unstable compounds from which H_2O is eliminated leaving unsaturated compounds which polymerize.
2. Addition of O_2 to form carboxyl derivatives from which CO_2 is eliminated followed again by polymerization.
3. Formation and elimination of volatile oxidation products other than H_2O and CO_2 followed again by polymerization.

It is worth noting, that the best crudes for asphalt air blowing are those with high percentage of asphaltene fraction and low in paraffin hydrocarbons, and waxes. Resins can be oxidized to asphaltenes relatively easily, so crudes rich in resin are good raw materials for asphalt manufacture. Oils can also be oxidized to asphaltenes, but they must be oxidized to resins first, which requires a more severe operation. Cracked residua simply do not make good asphalt.

Assay: The crude

The crude oil assay is a compilation of laboratory and pilot plant data that define the properties of the specific crude oil. At a minimum, the assay should contain a distillation curve for the crude and a specific gravity curve. Most assays however contain data on pour point (flowing criteria), sulfur content, viscosity, and many other properties. The assay is usually prepared by the company selling the crude oil, it is used

extensively by refiners in their plant operation, development of product schedules, and examination of future processing ventures. Engineering companies use the assay data in preparing the process design of petroleum plants they are bidding on, or having been awarded the project, they are now building.

The data normally contained in a well produced assay will be:

- A TBP curve
- A specific gravity curve
- A sulfur content curve
- A pour point and cloud point curve
- Product tables of some of the lighter products. These should contain at least the following:
  - ➢ The product boiling range
  - ➢ The product yield on crude
  - ➢ The cuts gravity (usually in °API)
  - ➢ A PONA (paraffin, olefin, naphthene, and aromatic content)
  - ➢ In the case of the naphthas the cuts octane values
  - ➢ In the case of kerosene cuts, their sulfur and smoke point data
  - ➢ In the case of diesel and gas oil cuts their diesel index or cetane value

Full details of a typical Assay and a description of the tests and data are given in Chapter 1 of this Handbook.

ASTM (American Standard Testing Methods)

The tests and test methods provided by this body define and establish the quality of petroleum products and provide data on petroleum intermediate streams. This later provision is used as a basis for refinery planning, operation, and engineering work associated with the refinery. Among the more important tests are those given below:

- D56—Tag Closed Flash Point (The Abel Flash)
- D86—Standard Test For Distillation of Petroleum Products
- D93—The Pensky Marten Flash Point Closed Cup Test
- D97—Cloud & Pour Points
- D129—Sulfur Content (Bomb Method)
- D189—Condradson Carbon Content
- D323—Reid Vapor Pressure
- D445—Kinematic Viscosity
- D613—Cetane Number
- D908—Octane Number Research
- D1160—Gas oil Distillation (Sub Atmospheric)

- D1298—Specific Gravity (by hydrometer)
- D1837—Weathering Test for LPGs
- D2163—Component Analysis of LPGs (by gas chromatography)

These are the most common tests to define marketable quality and in plat operation control. Further details are given in Chapter 7 of this Handbook.

Atmospheric crude distillation unit

History of the process

The distilling of petroleum products from crude oil to some extent or other has long been practiced. Certainly, the ancient Egyptians, Greeks, and Romans had some form of extracting a flammable oil from, probably, weathered crude oil seepage. It wasn't though until the turn of the nineteenth and twentieth century that crude oil well drilling was first discovered and commercialized. Originally the crude oil was refined to produce essentially Kerosene (Lamp Oil), and a form of gasoline known then as benzene (as opposed to benzene already being produced from coal) and the residue used as pitch for calking and sealing. The lamp oil or kerosene was produced to provide a means of illumination, later a lighter cut known as Naphtha was produced for the same purpose but used in special pressurized lamps.

The production of these early distillates was by made by cascading the crude oil through successive stills each operating at successively higher temperatures. This is shown in diagram Figure 19.A.8. This is described more fully in Chapter 3 of this Handbook.

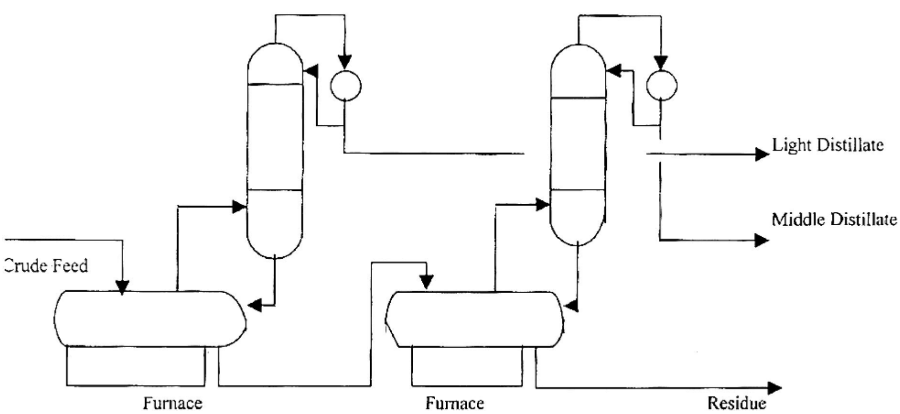


Figure 19.A.8. Schematic of a continuous atmospheric crude still.

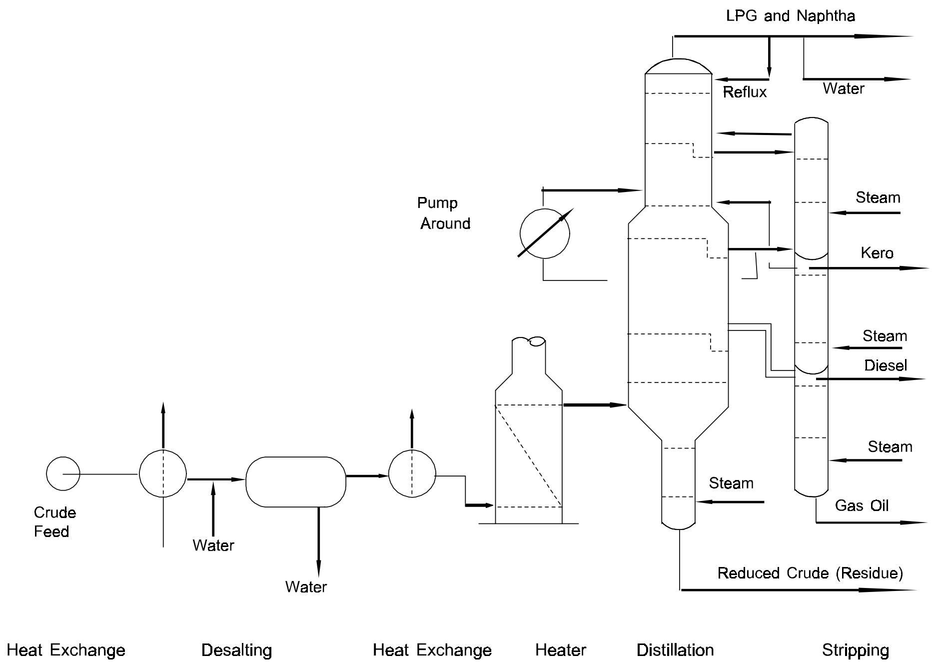


Figure 19.A.9. A Typical atmospheric crude distillation unit.

The major breakthrough in this process was the development of the single fractionating column. This came in the late 1920s and 1930s. In many refineries however, even in some modern ones built after say 1960, the atmospheric crude unit contains a primary fractionator which removes the light ends and some naphtha, before the main tower. These cases are rare and are only used when the crude feed contains a great deal of light ends (spiled crude) or a primary tower is added to increase throughput.

The process

Crude oil is pumped from storage to be heated by exchanges against hot overhead and product streams in the crude unit. At a temperature of about 200–250°F, the crude enters the desalter. Free salt water contained in the crude is washed out and separated by means of an electrostatic precipitator contained in the desalter drum. The water phase from the drum is sent to a sour water stripper to be cleaned before disposal to the oily water sewer.

The oil phase is further heated by exchange with hot sidestream and bottom products before entering a fired heater. The crude oil is heated in the heater to a temperature that will vaporize the distillate products in the crude tower. Some additional heat is

added to the crude to vaporize about 5% more than required for the distillate streams. This is called overflash and is used to ensure good reflux streams in the tower.

The un-vaporized portion of the crude leaves the bottom of the tower via a steam stripper section as the bottom product. The distillate vapors move up the tower counter current to the cooler liquid reflux streams coming down. Heat and mass transfer take place on the trays contained in the tower. Distillate products are removed from the various sections of the tower, they are stream stripped and sent to storage. The full naphtha vapor is allowed to leave the top of the tower to be condensed and collected in the overhead drum. A portion of this stream is returned as reflux while the remainder is delivered to the light end processes for stabilizing and further distillation.

The side-stream distillates shown in Figure 19.A.9 above are:

- Heavy Gas Oil (has the highest Boiling Point)
- Light Gas Oil (will become Diesel)
- Kerosene (will become Jet Fuel)

A "Pump around" section is included at the light gas oil draw-off. This is simply an internal condenser which takes heat out of that section of the tower. This in turn ensures a continued reflux stream flow below that section.

B

Barrels

In the petroleum industry, the barrel is a standard form of measuring liquid volume. A barrel of oil is defined as 42 U.S. gallons (one U.S. gallon equals 231 cubic inches). It is still used extensively in most countries, but is being replaced particularly in European countries by the metric measures of cubic meters or liters, or by weight measures like kg or tonnes (1000 kg).

BPCD and BPSD

BPCD is the measure of throughput or stream flow based on an operation over one year of 365 days. BPSD is the rated throughput of a plant or the rate of a stream over the total operating days in the year. BPCD is barrels per calendar day, and BPSD is barrels per stream day. BPSD is defined as BPCD divided by the service factor as a fraction. The service factor is the percentage time over a calendar year that the unit is operating. Each type of unit is allocated a service factor depending on the amount of scheduled shut down time the particular unit requires over the year for maintenance. The following is an example of some service factors:

Unit	Service Factor Percent
Crude distillation unit	95–98
Light ends distillation	98
Vacuum crude distillation	95–98
Visbreaker and thermal cracker	90
Cat reformer	90–92
Naphtha hydrotreaters	90–92
Gas oil hydrotreaters	90
Fluid catalytic crackers	85–90
Hydrocrackers (distillate feed)	90
Hydrocrackers (residue feed)	80–82 (includes residue hydrotreating)
Cokers	85

These service factors are based on modern day plant operating controls and state of the art catalyst quality and regenerating frequency.

Base lube oils

This refers to a lube product that meets all lube specifications and is suitable for blending to meet performance specifications.

Bitumen

Bitumen is the term often given to untreated asphalt from the vacuum distillation of crude and the extract from the de-asphalting unit. This is before the stream has been treated, with cut backs or by air blowing to make the various asphalt product grades.

Boiling points and boiling range

It is not possible to separate the components of crude oil into individual chemical compounds. However groups of these component mixtures are grouped together and identified by the boiling point at atmospheric pressure of the lightest component in the group and the boiling point of the heaviest component in the group. The group itself is called a *Cut* and the range of temperatures that identify it is called the boiling range or cut range. These can be related to the crude TBP curve to determine its yield on that particular crude (see Chapter 1 of this Handbook).

Bright stocks (lube oils)

These are processed from the raffinate of the vacuum residue de-asphalting unit.
(See Chapter 12 of this Handbook)

Bromine number

The Bromine number of petroleum distillates is determined by Electrometric Titration in accordance with ASTM laboratory test D 1159. It is measure of olefins in the sample according to the equation:

$$\% \text{ Olefins} = \frac{\text{Bromine number} \times \text{Mole weight of olefins}}{160}$$

Bubble points

Bubble point—is the temperature and pressure at which a hydrocarbon begins to boil.

The overhead from a fractionator has the following composition:

Mole fraction composition:

C_2	0.008
C_3	0.054
iC_4	0.021
nC_4	0.084
C_5s	0.143
C_6	0.155
C_7	0.175
Comp 1	0.124
Comp 2	0.124
Comp 3	0.075
Comp 4	0.037
Total	1.000

The components 1–4 are pseudo components that have properties similar to real components with the same boiling point. The mid boiling points of these components are:

	°F
Comp 1	260
Comp 2	300
Comp 3	340
Comp 4	382

The reflux drum temperature will be fixed at 100°F. The pressure will be calculated at *the bubble point* of this material at 100°F.

Bubble point is defined as the sum of all y's = sum of all Kx's.

x is the mole fraction of a component in the liquid phase and y is the mole fraction of the component in the vapor phase at equilibrium. At bubble point $\Sigma y = \Sigma Kx$.

K is the equilibrium constant and can be read from the curves found in text books such as Maxwell's *Data book on Hydrocarbons* or can be considered (rough and not be used for definitive design) as:

$$\frac{\text{Vapor Pressure}}{\text{Total Pressure}} = K$$

This relationship will be used for this calculation.

The calculation is iterative (trial and error) as follows:

AT 100°F

		1st Trial @ 5 psig		2nd Trial @ 10 psig	
	Mol fract. X	K	$Y = KX$	K	$Y = KX$
C_2	0.008	40.6	0.325	32.4	0.259
C_3	0.054	9.3	0.502	7.42	0.401
iC_4	0.021	3.55	0.075	0.38	0.05
nC_4	0.084	2.54	0.213	0.03	0.171
C_5	0.143	0.89	0.127	0.71	0.102
C_6	0.155	0.254	0.039	0.20	0.031
C_7	0.175	0.084	0.015	0.067	0.011
Comp 1	0.124	0.023	0.003	0.020	0.002
Comp 2	0.124	NEG	NEG		
Comp 3	0.075	NEG	NEG		
Comp 4	0.037	NEG	NEG		
	1.000		1.299		1.027

For 2nd trial (Estimate)

Take the K value of the highest fraction of y (in this case C_3) where $K = 9.3$.
Take this $K = 7.16$ (new K)
1.299

Make the 2nd trial with KC_3 at 7.16 which gives a systems pressure P as follows:

VP C3 = 7.1 where VP C3 @ 100°F is 190 psia

$$\text{Then } P = \frac{190}{7.1} = 26.5 \text{ psia.}$$

2nd trial pressure = 26.5 psia = 11.8 psig
Lets set it at 12 psig.

The second trial gives sum of Y's $= 1.027$ and this is considered close enough to 1.000. Then the drum will be operated at 100°F and at 12 psig.

Burners

The purpose of a burner is to mix fuel and air to ensure complete combustion. There are about 12 basic burner designs. These are:

Direction	—	vertical up fired
		vertical down fired
		horizontally fired
Capacity	—	high
		low
Fuel type	—	gas
		oil
		combination
Flame shape	—	normal
		slant
		thin, fan-shaped
		flat
		adaptable pattern
Hydrogen content	—	high
Excess air	—	normal
low		
Atomization	—	steam
		mechanical
		air assisted mechanical
Boiler types		
Low NO_x		
High intensity		

Various combinations of the above types are available.

Gas burners

The two most common types of gas burners are the "pre-mix" and the "raw gas" burners.

Pre-mix burners are preferred because they have better "linearity", i.e., excess air remains more nearly constant at turndown. With this type, most of the air is drawn in through an adjustable "air register" and mixes with the fuel in the furnace firebox. This is called secondary air. A small part of the air is drawn in through the "primary

air register" and mixed with the fuel in a tube before it flows into the furnace firebox. A turndown of 10 : 1 can be achieved with 25 psig hydrocarbon fuels. A more normal turndown is 3 : 1.

Oil burners

An oil burner "gun" consists of an inner tube through which the oil flows and an outer tube for the atomizing agent, usually steam. The oil sprays through an orifice into a mixing chamber. Steam also flows through orifices into the mixing chamber. An oil-steam emulsion is formed in the mixing chamber and then flows through orifices in the burner tip and then out into the furnace firebox. The tip, mixing chamber and inner and outer tubes can be disassembled for cleaning.

Oil pressure is normally about 140–150 psig at the burner, but can be lower or higher. Lower pressure requires larger burner tips, the pressure of the available atomizing steam may determine the oil pressure.

Atomizing steam should be at least 100 psig at the burner valve and at least 20–30 psi above the oil pressure. Atomizing steam consumption will be about 0.15–0.25 lbs steam/lb oil, but the steam lines should be sized for 0.5.

Combination burners

This type of burner will burn either gas or oil. It is better if they are not operated to burn both fuels at the same time because the chemistry of gas combustion is different from that of oil combustion. Gases burn by progressive oxidation and oils by cracking. If gas and oil are burned simultaneously in the same burner, the flame volume will be twice that of either fuel alone.

Pilots

Pilots are usually required on oil fired heaters. Pilots are fired with fuel gas.

Pilots are not required when heaters are gas fired only, but minimum flow bypasses around the fuel gas control valves are used to prevent the automatic controls from extinguishing burner flames.

Excess air and burner operation

The excess air normally used in process fired heaters are about 15–25% for gas burners and about 30% for oil burners. These excess air rates permit a wide variation in heater firing rates which can be effectively controlled by automatic controls without fear of 'Starving' the heater of combustion air. There has been considerable work lately to

reduce this excess air considerably mostly to minimize air pollution. This practice has not been used in process heaters to date. It has however been adopted in the operation of large power station type heaters with some success.

Normally, companies specify that burners be sized to permit operation at up to 125% of design heat release with a turndown ratio of 3 : 1. This gives a minimum controllable rate of 40% of design without having to shut down burners.

Burner control

Burner controls become very important from safety and operation considerations. Most systems include an instrumentation system with interlocks that prohibit:

- Continuing firing when the process flow in the heater coil fails
- The flow of fuel into the firebox on flame failure

Under normal operating conditions the amount of fuel that is burnt is controlled by flow controllers operated on the coil outlet temperature. With combination burners the failure of one type of fuel automatically introduces the second type. Such a switch over can also be affected manually. This aspect is usually activated on pressure control of the respective the fuel system. That is on low pressure being sensed on the fuel being fired automatically switches to the second fuel.

(See Chapter 18 for more details on burners and heaters.)

Heater noise

All heaters are noisy and this noise is the result of several mechanisms. Among these are the operation of the burners. Gas burners at critical flow of fuel emit a noise. This can be minimized by designing for low pressure drop in the system. Intake of primary and secondary air is another source of noise. Forced draft burners are generally quieter than natural draft if the air ducting is properly sized and insulated. The design of the fan can also reduce noise in this mechanism. Low tip speed fan favors low noise levels.

C

Catalytic reforming unit

History. Without doubt, the development of catalytic reforming was a major evolution of the petroleum refining industry. It, in fact signified the birth of the 'Hydroskimming

Refinery'. The process produces hydrogen as a by-product in the upgrading of the naphtha octane value, and this hydrogen provided the means to upgrade a number of products by hydro treating.

Catalysts had been used during World War II for the upgrading of aviation fuels in terms of their octane number. Catalytic reforming of a kind had also been developed from a coal usage plant to process the aromatics used for war time explosives, etc. It was in the late 1950s and early 1960s that the fixed bed of bi-metallic catalyst was first developed. This process accomplished what the modern day catalytic reformers do in converting the cycloparaffins to their corresponding aromatics with the release of hydrogen molecules.

The process. Catalytic reforming is a process for improving the octane quality of straight-run naphthas and of mixed naphthas containing cracked naphtha. The principal reaction is dehydrogenation of naphthenes to aromatics. Contributing to the high octane of the product are side reactions such as hydrocracking of high-boiling hydrocarbons to low-molecular weight paraffins, isomerization of paraffins to branched-chain structures, and dehydrocyclization of paraffins and olefins to aromatics. Hydrogen recycle reduces the formation of carbon. Figure 19.C.1 is a process sketch of a typical catalytic reformer.

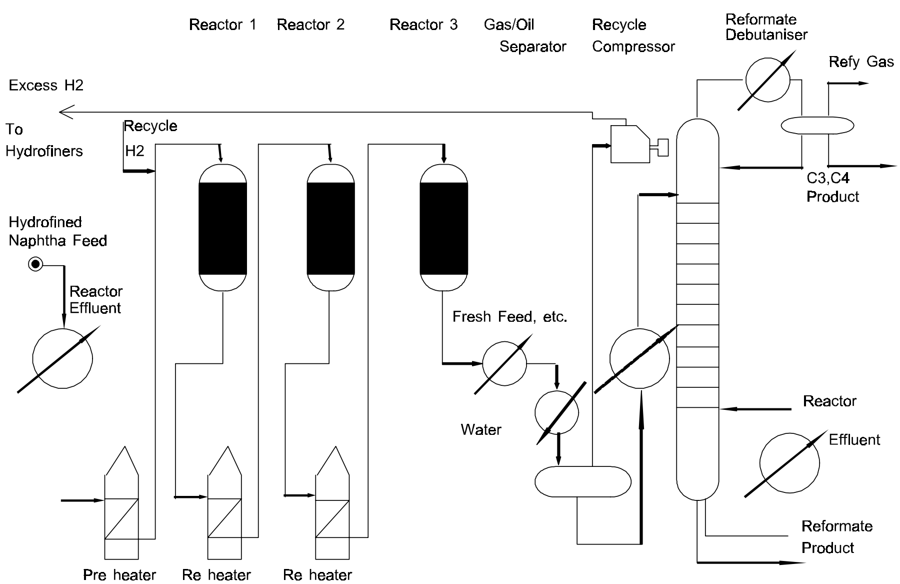


Figure 19.C.1. A typical catalytic reforming unit.

Feedstocks preferably are within the 200–430°F (TBP) boiling range. Feeds with lower initial boiling-point contain C_5 naphthenes which do not aromatize well. Feeds with higher final boiling point:

(a) Cause excessive lay-down of carbon on catalyst.
(b) Necessitate product re-running because reforming may increase the final boiling-point beyond gasoline specification.

The water content of the feedstock must be under 10 ppm to prevent rapid stripping of chloride from the platinum catalyst. Poisoning of the platinum catalyst is prevented by hydrofining the feed to a sulfur content below 10 ppm. Recycle hydrogen is added to the reformer feed and the mixture is preheated and charged to the first of a series of reactors. As the reactions are highly endothermic, each reactor effluent is reheated before being charged to the following reactor.

The effluent from the final reactor is separated into hydrogen rich gas and reformate. With heavy feeds, the reformate may contain 430°F + polymer.

The catalyst, 0.6 wt% platinum and 0.6 wt% chloride on alumina base, is regenerable. The type of regeneration system and the cycle length between regeneration periods depends on feed quality and reforming severity. Good feedstock quality and reforming severity favor the use of the semi-regeneration system, in which the plant is shut down after three months of operation to regenerate all reactors simultaneously. When reforming poorer feed and/or going into higher octane, the cyclic regenerative system is used in which there is a spare or "swing" reactor. A deactivated reactor can be regenerated in one day without process interruption. Many units now operate at high severity with continuous catalyst regeneration (CCR). Further details at this process are given in Chapter 5.

Centrifugal compressors

Compressors are divided into four general types, these are:

- Centrifugal
- Axial
- Reciprocating
- Rotary

This item refers only to the centrifugal compressor a description of which now follows.

This type of compressor consists of an impeller or impellers rotating at high speed within a casing. Flow is continuous and inlet and discharge valves are not required as part of the compression machinery. Block valves are required for isolation during maintenance.

Centrifugal compressors are widely used in the petroleum, gas, and chemical industries primarily due to the large volumes of gas that frequently have to be handled. Long continuous operating periods without an overhaul make centrifugal compressors desirable for use in petroleum refining and natural gas applications. Normally they are considered for all services where the gas rates are continuous and above 400 ACFM (actual cubic feet per minute) for a clean gas, and 500 ACFM for a dirty gas. These rates are measured at the discharge conditions of the compressor. Dirty gases are considered to be gases similar to those from a catalytic cracker, which may contain some fine particles of solid or liquid material.

The slowly rising head capacity performance curves make centrifugal compressors easy to control by either suction throttling or variable speed operation.

The main disadvantage of this type of compressor is that it is very sensitive to gas density, molecular weight, and polytropic compression exponent. A decrease in density or molecular weight results in an increase in the polytropic head requirement of the compressor to develop the required compression ratio.

The flow range of centrifugal compressors is as shown in Table 19.C.1.

In general, the head or differential pressure levels served by centrifugal compressors is considerably lower than that for reciprocal. The following diagram illustrates this feature (Figure 19.C.2).

Surge. A characteristic peculiar to centrifugal and axial compressors is a minimum capacity at which the compressor operation is stable. This minimum capacity is referred to as the surge or pumping point. At surge, the compressor does not meet the pressure of the system into which it is discharging. This causes a cycle of flow reversal as the compressor alternately delivers gas and the system returns it.

Table 19.C.1. Centrifugal compressor flow range

Nominal flow range (inlet acfm)	Average polytropic efficiency	Average adiabatic efficiency	Speed to develop 10,000 ft head/wheel
500–7,500	0.74	0.70	10,500
7,500–20,000	0.77	0.73	8,200
20,000–33,000	0.77	0.73	6,500
33,000–55,000	0.77	0.73	4,900
55,000–80,000	0.77	0.73	4,300
80,000–115,000	0.77	0.73	3,600
115,000–145,000	0.77	0.73	2,800
145,000–200,000	0.77	0.73	2,500

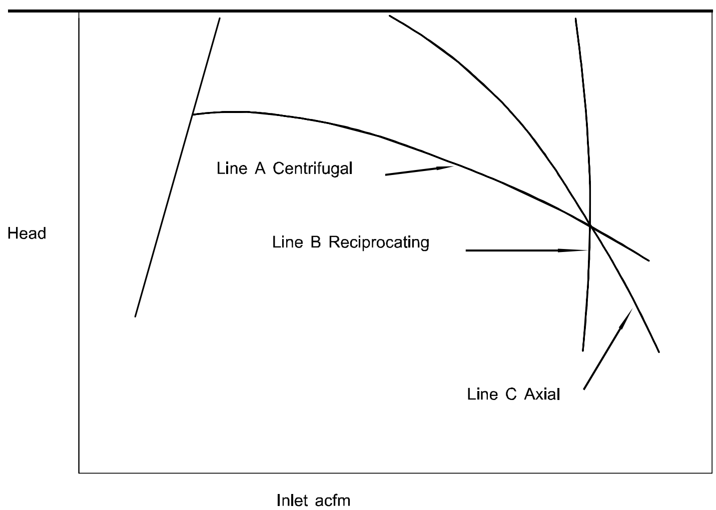


Figure 19.C.2. Comparison of differential compressor heads.

The surge point of a compressor is nearly independent of its speed. It depends largely on the number of wheels or impellers in series in each stage of compression. Reasonable reductions in capacity to specify for a compressor are shown in Table 19.C.2.

An automatic re-circulation bypass is required on most compressors to maintain the minimum flow rates shown. These are required during start-up or when the normal load falls below the surge point. Cooling is required in the recycle circuit if the discharge gas is returned to the compressor suction.

Performance curves for centrifugal compressors

The rise of performance curves should be specified for a compressor. This is normally done by specifying the pressure ratio rise to surge required in each stage of compression. A continuously rising curve from normal flow rate to surge flow is required for stable control.

Table 19.C.2. Effect of capacity reduction

Wheels/compression stage	% of Normal capacity at surge-maximum
1	55
2	65
3 or greater	70

The pressure ratio rise to surge is largely a function of the number of impellers per compression stage. Reasonable pressure ratio rises to specify are shown below:

Wheels/compression stage	Minimum % of rise in pressure ratio from normal to surge flow
1	$3\frac{1}{2}$
2	6–7
2 or greater	$7\frac{1}{2}$

Frequently, the performance curves for a compressor have to be plotted to determine if all anticipated process operations will fit the compressor and its specific speed control. Three points on the head capacity curve are always known. These are the normal, surge, and maximum capacity points. The normal capacity is always considered to be on the 100% speed curve of the compressor. The surge point and the compression ratio rise to surge have been specified. From this the head produced by the compressor at the surge point can be back-calculated using the head-pressure ratio relationship. The maximum capacity point is specified to be at least 115% of capacity at 85% of normal head.

The head capacity curve retains its characteristic shape with changes in speed. Curves at other speeds can be obtained from the three known points on the 100% speed curve by using the following relationships:

1. The polytropic head varies directly as the speed squared.
2. The capacity varies directly as speed.
3. The efficiency remains constant.

Figure 19.C.3 below shows a typical centrifugal compressor performance curve.

Cloud points

The cloud point of a transparent or semi transparent oil sample is the temperature at which a cloud or mist forms in the sample. The method is ASTM D 2500, and is carried out in the laboratory where a sample of the oil is reduced in temperature by submerging the sample in its container first in ice then in iced salt and finally in a solid CO_2 bath. The container is a cylindrical glass vessel about 19 mm diameter by 100 mm deep. The vessel is filled to a mark about 80 mm deep and a low range thermometer inserted so the bulb is about 10–12 mm below the sample surface. Temperature readings are taken at every stage. Readings are more frequently taken in the last cooling stage and that temperature at which the sample becomes misty is taken as its cloud point.

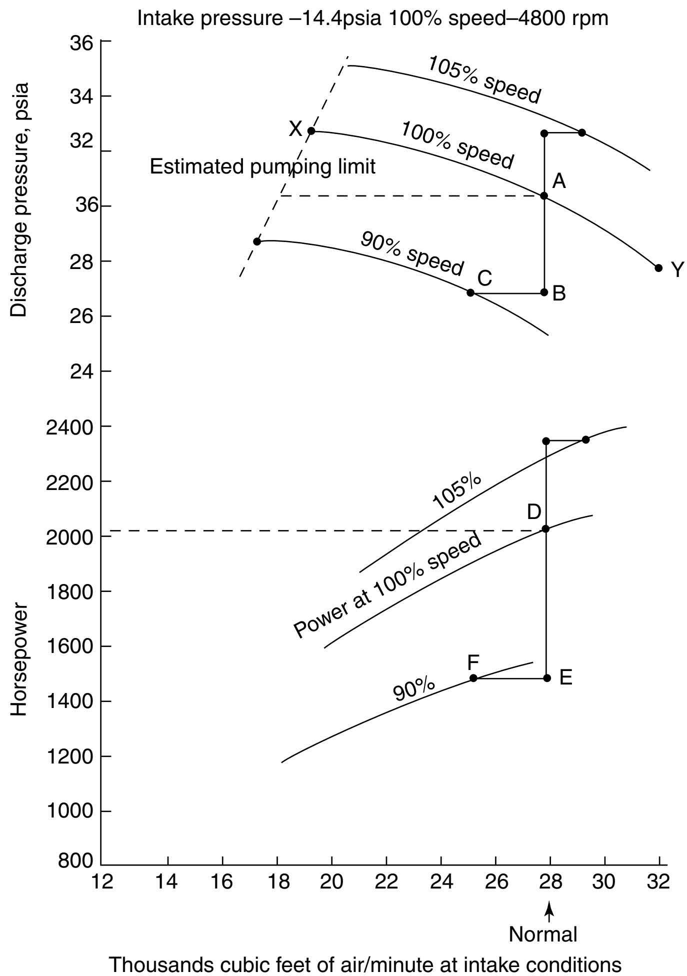


Figure 19.C.3. Typical performance curves for a centrifugal compressor.

Coke

Coke is formed in the processes to convert the residuum fuels to the more desirable distillate products of naphtha and lighter through to the middle distillates. By far the largest production of coke is the sponge coke from the delayed coking process. Uncalcined sponge coke has a heating value of about 14,000 Btu/lb and is used primarily as a fuel. High sulfur sponge coke however is popular for use in cement plants since the sulfur reacts to form sulfates. Sponge coke is calcined to produce a coke grade suitable for anodes in the aluminum industry.

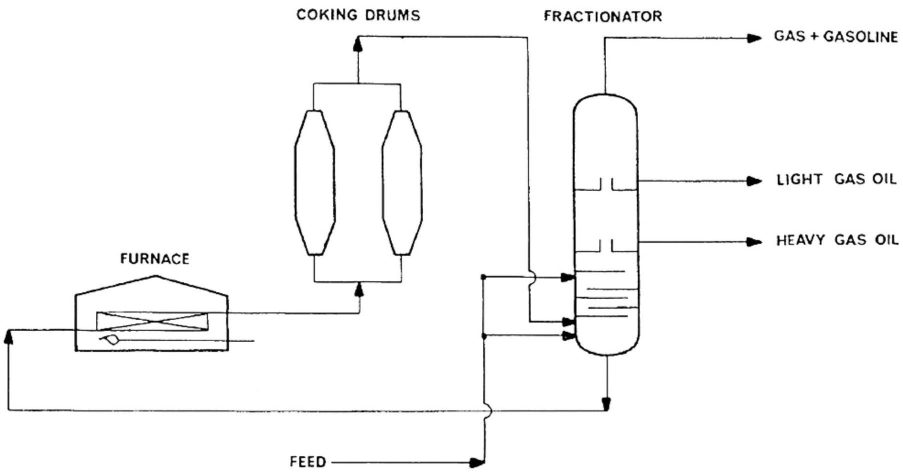


Figure 19.C.4. A delayed coker.

Coking processes

Coke is formed in the processes to convert the residuum fuels to the more desirable distillate products of naphtha and lighter through to the middle distillates. There are two routes by which this coking process proceeds. The first and the most common is the delayed coking route. The second is the fluid coking method, and this has been made more attractive to many refiners with the development of ExxonMobil's proprietary process of *Flexicoking*. This proprietary process eliminates the coke completely by converting it to low Btu fuel gas (see Chapter 11).

The delayed coking process

The delayed coking process is illustrated in Figure 19.C.4.

The fuel oil or heavy oil feed is routed to a cracking furnace similar to other thermal cracking processes. The effluent from the furnace is sent to one of a set of several coking drums without quenching. The effluent is normally at a coil outlet temperature of around 920°F and at a pressure of 30–50 psig and the coking drum is filled in about 24 hr. The vapors leaving the top of the drum whilst filling are routed to the fractionator, where they are fractionated to the distillate products. The very long residence period of the effluent in the coking drums results in the complete destruction of the heavy fractions, and a solid residue rich in carbon is left in the drum as coke. When the drum is full of coke it is cooled and the top and bottom of the drum are opened. Special high-pressure water jets are used to cut and remove the coke through the drum's bottom opening.

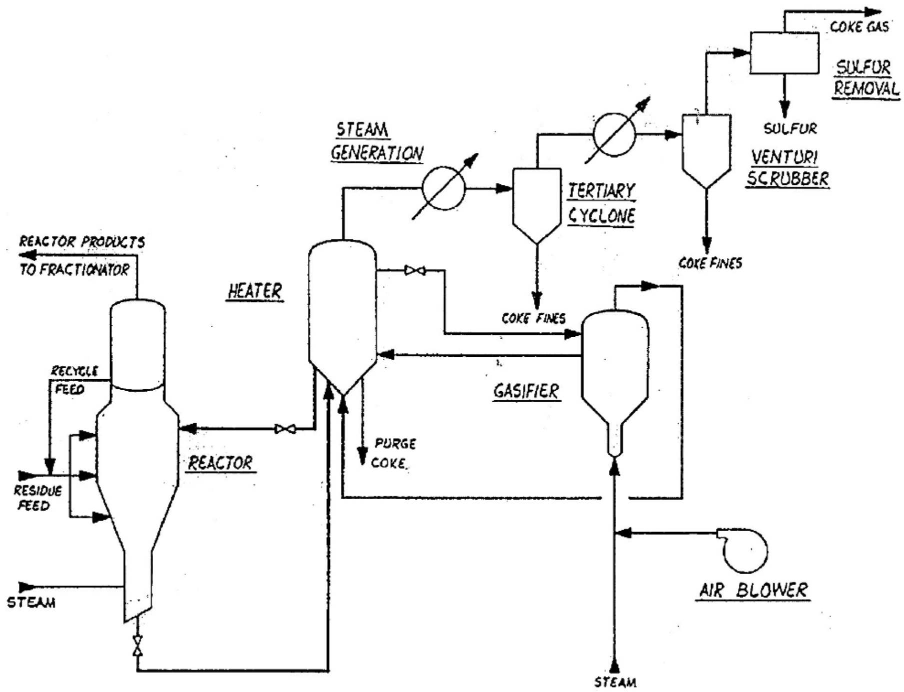


Figure 19.C.5. A flexi (fluid) coking process.

Flexi coking (Fluid coker)

Flexi-coking is a thermal conversion process licensed by Exxon Research and Engineering Company. The process itself is an extension of the traditional fluid coking process. The extension allows for the gasification of the major portion of the coke make to produce a low-Btu gas. The gasification step follows closely to the concept used in the coal gasification processes.

Figure 19.C.5 is a simplified flow diagram of the Flexi-coking process.

Heavy residuum feed is introduced into the reactor vessel where it is thermally cracked. The heat for cracking is supplied by a fluidized bed of hot coke transferred to the reactor from the heater vessel.

The vapor products of the reaction leave the reactor zone to enter the scrubber section. Fine coke and some of the heavy oil particles are removed from the cracked products in the scrubber zone and returned to mix with the fresh feed entering the reactor. The reactor products subsequently leave the scrubber and are routed to a conventional fractionating facility. Steam is introduced to the bottom of the reactor to maintain a

fluid bed of coke and to strip the excess coke leaving the reactor free from entrained oil. The coke leaving the reactor enters the heater vessel, where sufficient coke is converted into CO/CO_2 in the presence of air. This conversion of the coke provides the heat for cracking which is subsequently transmitted to the reactor by a hot coke stream. The net coke make leaves the heater and enters the gasifier vessel. Air and steam are introduced into the gasifier to react with the coke producing a low-Btu gas consisting predominately of hydrogen, CO, CO_2, and nitrogen. This gas together with some excess air is transferred to the heater, and leaves this vessel to be suitably cleaned and cooled.

Flexi-coking is an extinctive process. By continuous recycle of heavy oil stream all the feed is converted into distillate fractions, refinery gas, and low Btu gas. There is a very small coke purge stream which amounts to about 0.4–0.8 wt% of fresh feed. When suitably hydrotreated, the fractionated streams from the Flexi-coker provide good quality products. Hydrotreated coker naphtha provides an excellent high naphthene feed to the catalytic reformer.

Cold flash separator

In many high temperature and high pressure hydrocracker or hydrotreater units the reactor effluent is reduced in pressure and temperature in several stages. The last of these stages is the cold flash separation stage. Figure 19.C.6 shows a typical residuum hydrocracker with a cold flash separator.

The reactor effluent leaves the reactor to enter a hot flash drum which is near to the reactor pressure and temperature conditions. Here the heavy bituminous portion of the effluent leaves from the bottom of the drum while the lighter oil and gas phase leaves as a vapor from the top of the drum. This vapor is subsequently cooled by heat exchange with the feed and further cooled and partially condensed by an air cooler. This cooled stream then enters a cold separator operating at a pressure only slightly lower than that of the reactor. A rich hydrogen gas stream is removed from this drum to be amine treated and returned as recycle gas to the process. The distillate liquid leaves from the bottom of the separator to join a vapor stream from the hot flash surge drum (in this case a thermal cracker feed surge drum). Both these streams enter the *cold flash drum* which operates at a much lower pressure than the upstream equipment. A gas stream is removed from the drum to be routed to the absorber in a light ends unit. The liquid distillate from the drum is routed to the debutanizer in the light ends unit.

Component balances

Component balances are derived from the TBP of the material requiring the balance. These component balances are derived by splitting the TBP into mid-boiling point

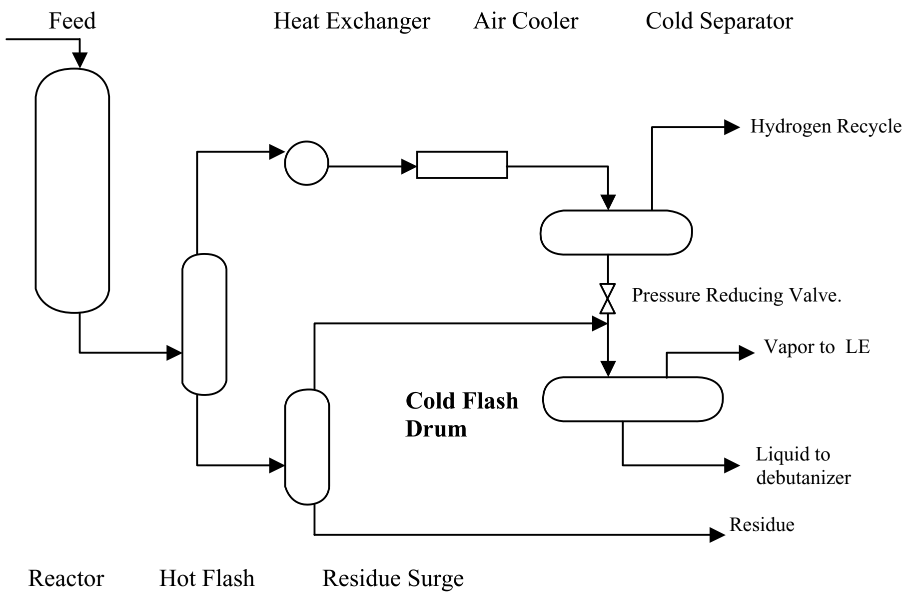


Figure 19.C.6. Typical residue hydrocracker with cold flash drum.

pseudo components (see Chapter 1 for definition of pseudo components and mid-boiling points). The purpose of component balances is to calculate more accurately fractions of the feed material properties in terms of specific gravity, sulfur content, mole weight, cloud and pour points and the like. Figure 19.C.7 shows a hypothetical TBP curve of a middle distillate fraction. This fraction has been broken up into 6 pseudo components, with mid boiling points of 410°–591°F. By referencing the crude feed assay from which this fraction originates, the SG of each component can be read off as °API. If it is a well-produced assay the component sulfur, cloud and pour points can also be read off for each pseudo component. The volume of each pseudo component forming the fraction is shown as the 'x' of the TBP curve.

Some of the components shown in the diagram are tabled in order to determine the fraction's properties. Table 19.C.3 is an example of the purpose of the component breakdown In this case only the specific gravity is determined, but by applying the respective assay data for other properties a reasonable definition of the fraction can be obtained (see Chapter 1).

Condensers (shell and tube)

In the chemical process plants vapors are condensed either on the shell side of a shell and tube exchanger, the tube side of an air cooler, or by direct contact with the coolant

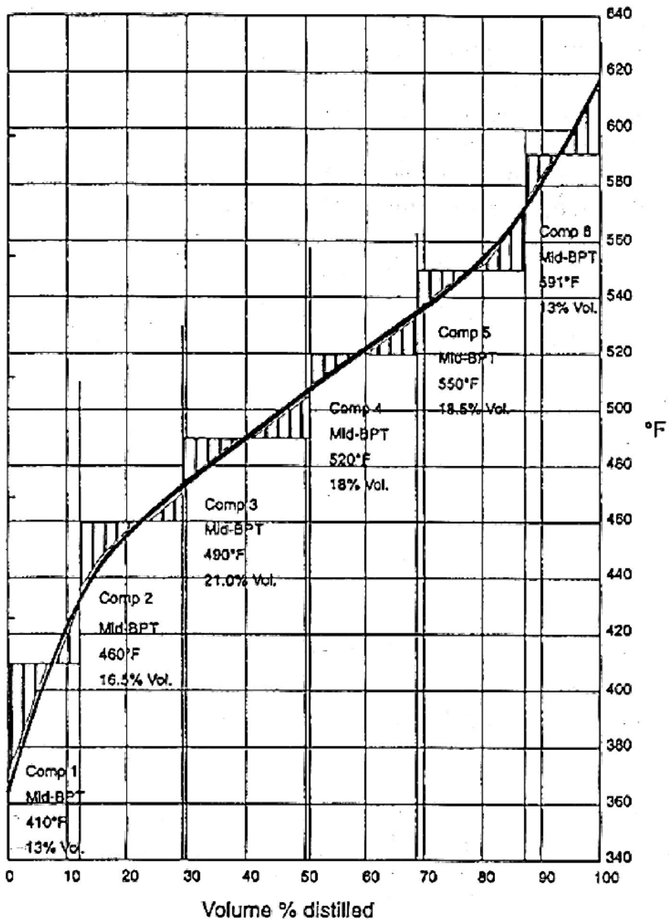


Figure 19.C.7. A Typical component breakdown.

in a packed tower. By far the most common of these operations are the first two listed. In the case of the shell and tube condenser, the condensation may be produced by cooling the vapor by heat exchange with a cold process stream or by water. Air cooling has overtaken the shell and tube condenser in the case of water as coolant in popularity as described in item 6.4.

In the design or performance analysis of condensers the procedure for determining thermal rating and surface area is more complex than that for a single phase cooling and heating. In condensers there are three mechanisms to be considered for the rating procedure. These are:

Table 19.C.3. Determination of SG using components

Component	Volume %	Mid BPt °F	SG @ 60°F (From assay)	Weight factor
1	13.0	410	0.793	10.3
2	16.5	460	0.801	13.2
3	21.0	490	0.836	17.6
4	18.0	520	0.844	15.2
5	18.5	550	0.846	15.7
6	13.0	591	0.850	11.1
Totals	100.0			83.1

$$\text{SG @ } 60^{\circ}\text{F} = \frac{83.1}{100} = 0.831 \text{ or } 38.8^{\circ}\text{API.}$$

- The resistance to heat transfer of the condensing film
- The resistance to heat transfer of the vapor cooling
- The resistance to heat transfer of the condensate film cooling

Each of these mechanisms is treated separately and along pre-selected sections of the exchanger. The procedure for determining the last two of the mechanisms follows that for single-phase heat transfer. The following expression is used to calculate the film coefficient for the condensing vapor:

$$h_c = 8.33 \times 10^3 \times k_f \times \left[\frac{\text{Sg}_c}{\mu_f}\right]^{2.33} \times (M_c/L_c \cdot N_s)^{33}$$

where

h_c = Condensing film coefficient.
M_c = Mass condensed in lbs/hr
L_c = Tube length for condensation.
$= \frac{A_{\text{zone}}}{A} \times (L - 0.5)$
$N_s = 2.08\ \text{N}_t^{0.495}$ for triangular pitch.
k_f = Thermal conductivity of condensate at film temperature.
Sg = Specific gravity of condensate.
μ_f = Viscosity of condensate at film temperature (cP).

Again there are many excellent computer programs that calculate condenser thermal ratings, and these of course save the tedium of the manual calculation. However, no matter which method of calculation is selected there is required one major additional piece of data over that required for single-phase heat exchange. That item is the Enthalpy Curve for the vapor.

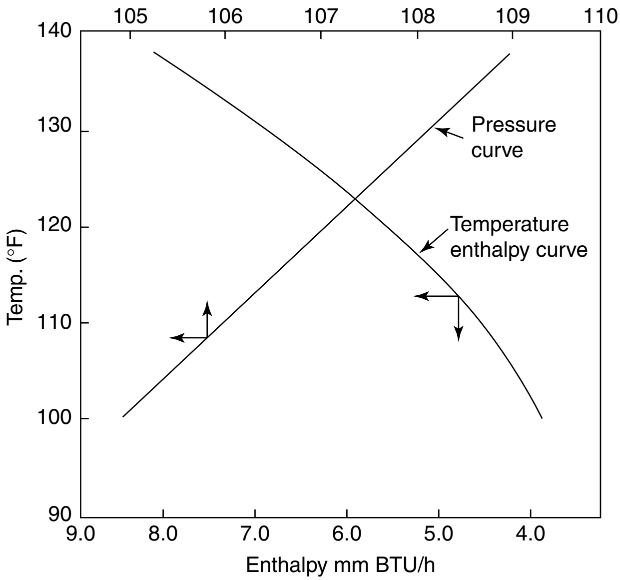


Figure 19.C.8. Typical enthalpy curves.

Enthalpy curves are given as the heat content per lb or per hour contained in the mixed phase condensing fluid plotted against temperature. An example of such a curve is given in Figure 19.C.8. These Enthalpy curves are developed from the vapor/liquid or flash calculations described in Chapter 1 and 3.

Briefly, the calculation for the curve commences with determining the dew point of the vapor and the bubble point of the condensate. Three or more temperatures are selected between the dew and bubble points and the V/L calculation of the fluid at these temperatures carried out. Enthalpy for the vapor phase and the liquid phase are added for each composition of the phases at the selected temperatures. These together with the enthalpy at dew point and bubble point are then plotted.

A manual calculation for condensers is described here. Again this is done to provide some understanding of the data required to size such a unit and its significance in the calculation procedure. Computer aided designs should however be used for these calculations whenever possible.

The following calculation steps describe a method for calculating the film coefficient of a vapor condensing on the shell side of a S&T exchanger. The complete rating calculation will not be described here as much of the remaining calculation is simply repetitive.

Step 1. Calculate the dew point of the vapor stream at its source pressure. Estimate the pressure drop across the system. Usually 3–5 psi will account for piping and the exchanger pressure drop. Calculate the bubble point of the condensate at the terminal pressure. Select three or more temperatures between dew point and bubble point and calculate the vapor/liquid quantities at these conditions of temperature and pressure.

Step 2. Calculate the enthalpy of the vapor and liquid at these temperatures. Plot the total enthalpies against temperature to construct the enthalpy curve. Establish the properties of the vapor phase and liquid phase for each temperature interval. The properties mostly required are specific gravity, viscosity, Mole wt, thermal conductivity and specific heats.

Step 3. In the case of a water cooler calculate the duty of the exchanger and the quantity of water in lbs/hr. Commence the heat transfer calculation by assuming an overall heat transfer coefficient, calculating the corrected LMTD, and the surface area.

Step 4. Using the surface area calculated in Step 3 define the exchanger geometry in terms of number of tube passes, number of tubes on the center line, shell diameter, baffle arrangement and the shell free flow area. Calculate also the water flow in feet per sec.

Step 5. Divide the exchanger into 3 or 4 zones by selecting the zone temperatures on the enthalpy curve. Calculate the average weight of vapor and the average weight of condensate in each zone. Using these averages calculate the average heat transferred for:

Cooling of the vapor Q_{v}
Cooling of the condensate Q_{L}

Condensing of the vapor which will be:
Total heat in the zone (from the enthalpy curve) plus the difference of Q_{v} and Q_{L}.

Step 6. Calculate the film coefficient for the tube side fluid.

Step 7. Starting with zone 1 and knowing the outlet temperature of the coolant fluid, the total heat duty of the zone, and the shell side temperatures calculate the coolant inlet temperature. Using this calculate the LMTD for the zone and, assuming a zone overall heat transfer coefficient U, calculate a surface area for the zone. Using this and the total exchanger area estimated in Step 4 establish L_c in feet.

Step 8. Calculate the condensing film coefficient from the equation given earlier. This will be an uncorrected value for h_c. This will be corrected to account for turbulence by the expression.

$$h_{\mathrm{c\,(corr)}} = h_{\mathrm{c}} \times (G_{\mathrm{v}}/5)^{0.7}$$

where

G_{v} = average vapor mass velocity in lbs/hr sqft

Step 9. Calculate the value of G_v using the free flow area allocated to the vapor γ_v. The following expressions are used for this:

$$\gamma_v = 1 - \gamma_L$$

$$\frac{1}{\gamma_L} = 1 + \frac{\text{Ave mass vapor}}{\text{Ave mass liquid}} \times (\mu_v/\mu_L)^{.111} \times (\rho_L/\rho_v)^{.555}$$

$$G_v = \frac{\text{Ave mass Vapor}}{25 \times \text{Free flow area} \times \gamma_v}$$

Step 10. Calculate the film coefficient h_v for the vapor cooling mechanism. This will be the procedure used for a single phase cooling. This is corrected to account for resistance of the condensate film by the expression:

$$\frac{1}{h_{v\,corr}} = \frac{1}{h_c} + \frac{1}{1.25\,h_v}$$

Step 11. Calculate the film coefficient for the condensate cooling mechanism for single phase cooling on the shell side. This is corrected for drip cooling that occurs over a tube bank.

$$\text{Drip cooling } h_{dc} = 1.5 \times h_c$$

and

$$h_{L\,corrected} = \frac{2 \times h_{dc} \times h_L}{h_{dc} + h_L}$$

where h_t = The inside film coefficient based on outside diameter as follows

$$h_t = \frac{300 \times (V_t \times \text{tube i/d in ins})^{0.8}}{\text{tube o/d in ins}}$$

and V_t = Linear velocity of tube side flow in ft/sec.

Step 12. Calculate the total zone film coefficient h_o using the following expression:

$$h_o = \frac{Q_{zone}}{\frac{Q_c}{h_c} + \frac{Q_v}{h_v} + \frac{Q_L}{h_L}}$$

where Q_c, Q_v, Q_L, are enthalpies for condensing, vapor cooling, and condensate cooling, respectively.

Step 13. Calculate the overall heat transfer coefficient neglecting the shell side coefficient from step 12. Thus:

$$\frac{1}{U_x} = r_o + r_w + r_{io} + R_{io}$$

where

r_o, r_w, r_{io} are fouling factors for shell fluid, wall, and tube side fluid, respectively.
R_{io} is the tubeside film coefficient calculated in Step 6.

Step 14. Calculate the overall heat transfer coefficient U_{zone} for the zone using the expression:

$$U_{zone} = \frac{h_o \times U_x}{h_o + U_x}$$

Check the calculated U against the assumed for the zone. Repeat the calculation if necessary to make a match.

Step 15. Calculate the zone area using the acceptable calculated U. Repeat Steps 7–14 for the other zones. The total surface area is the sum of that for each zone.

Conradson carbon (ASTM D-189)

See Chapter 16.

Control valves

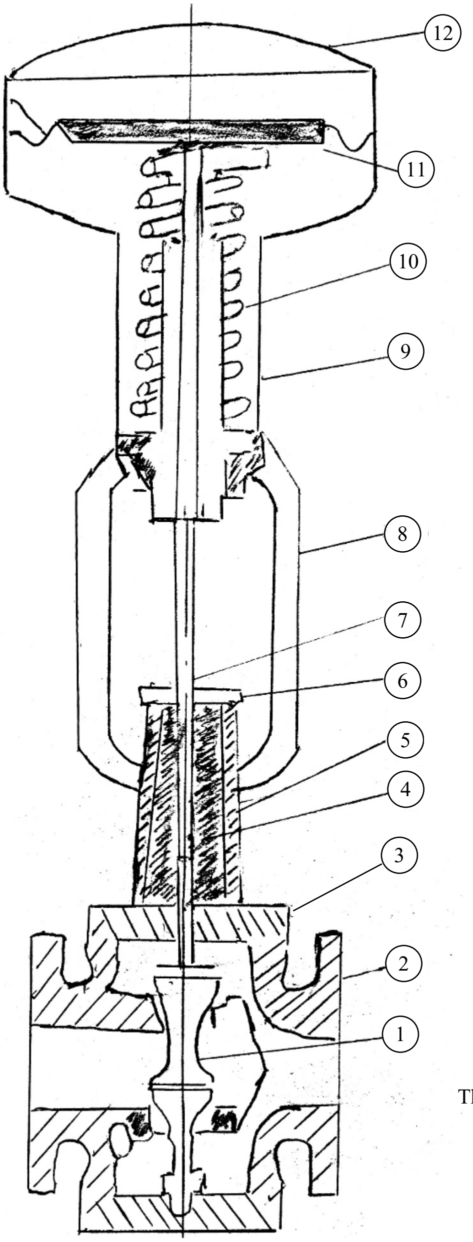
Control valves are used throughout the process and oil refining industries to control operating parameters. These parameters are:

- Flow
- Pressure
- Temperature
- Level

Figure 19.C.9 shows the conventional control valve which in this case is taken as a double seated plug type valve. Like most control valves it is operated pneumatically by an air stream exerting a pressure on a diaphragm which in turn allows the movement of a spring loaded valve stem. One or two plugs (the diagram shows two) are attached to the bottom of the valve stem which, when closed, fit into valve seats thus providing tight shut off. The progressive opening and closing of the plugs on the valve seats due to the movement of the stem, determines the amount of the controlled fluid flowing across the valve. The pressure of the air to the diaphragm controlling the stem movement is varied by a control parameter, such as a temperature measurement, or flow measurement, or the like.

There are two types of plug valves used for the conventional control valve function. These are:

- Single seated valves
- Double seated valves



1 INNER VALVE

2 BODY

3 BONNET

4 PACKING

5 STUFFING BOX

6 GLAND

7 VALVE STEM

8 YOKE

9 SPRING BARREL

10 SPRINGS

11 DIAPHRAM AND PLATE

12 DIAPHRAM DOME

The Conventional Control Valve

Figure 19.C.9. A doubled seated control valve.

Single seated valves are inherently unbalanced so that the pressure drop across the plug affects the force required to operate the valve. Double seated valves are inherently balanced valves and are the first choice in most services.

There are two other types of control valves in common service in the industry. These are the Venturi Type and the Butterfly type. Both these types when pneumatically operated (which they usually are) work in the same way as described above for a plug type valve. The major difference in these two types are in the valve system itself. In the case of the venturi the fluid being controlled is subjected to a 90° angle change in direction within the valve body. The inlet and outlet dimensions are also different, with the inlet having the larger diameter. The valve itself is plug type but seats in the bend of the valve body.

Venturi type or angle valves are used in cases where there exists a high-pressure differential between the fluid at the inlet side of the valve and that required at the outlet side. Details of these valves may be found in Chapter 13 of this book.

Butterfly valves operate at very low-pressure drop across them. They can operate quite effectively at only ins of water gauge pressure drop, and where the operation of the conventional plug type valves would be unstable. The action of this valve is by means of a Flap in the process line. The movement of this flap from open to shut is made by a valve stem outside the body itself. This stem movement, as in the case of the other pneumatically operated valves, is provided by air and spring loads onto the stem from a diaphragm chamber. The only major disadvantage in this type of valve is the fact that very tight shut off is difficult to obtain due to the flap type action of the valve. Details of valve characteristics and valve sizing are given in Chapter 13 of this book.

Cost estimating

Details of cost estimating as it applies to process plants including oil refineries are given in Chapter 17 of this book. The following is a synopsis of the cost estimate sections of Chapter 17.

The progress of any construction or development project in a refinery uses milestone cost estimates coupled with completion schedules for its measurement and control. In the life of a construction project therefore about four "control estimates" may be developed. For want of better terms these may be referred to as:

- The Capacity Factored Estimate
- The Equipment Factored Estimate
- The Semi Definitive Estimate
- The Definitive Estimate

These are described briefly as follows:

The capacity factored estimate

In most process studies this is the first estimate to be prepared. It is the one that requires the minimum amount of engineering but is the least accurate. This is because the plant that is used to factor from will not exactly match the plant in question. It is good enough however when comparing different processes where the estimates are on the same basis. Past installed costs of similar plants (Definitive Estimate) are used coupled with some experienced factors to arrive at this type of estimate. The cost of a higher or lower capacity plant is obtained from the equation:

$$C = K(A/B)^b$$

where

C = Cost of the plant in question.
K = Known cost of a similar plant of size B.
A = Is the capacity of the plant in question. (usually in vol/unit time).
B = Capacity of known plant.
b = Is an exponential factor ranging between 0.5 and 0.8.

The equipment factored estimate

This estimate requires a substantial amount of process engineering to define the specific plant or process that is to be estimated. Details of the degree of engineering that is to be performed is given in item 8.4. Briefly the following process activity is required:

- Development of a firm Heat and Material Balance
- An acceptable Process flowsheet to be developed
- An Approved Equipment list
- Equipment summary Process Data sheet for all major equipment
- Process Specification for Specialty Items

A detailed narrative giving a process description and discussion (This will be required for the management review and approval of the estimate).

The semi definitive and the definitive cost estimates

These estimates will include input from all engineering disciplines that are involved in the engineering and construction of the plant or process. Although major manufacturing companies such as large oil companies and chemical companies have sufficient statistical data to develop semi definitive and definitive estimates these are normally left to the engineering and construction companies.

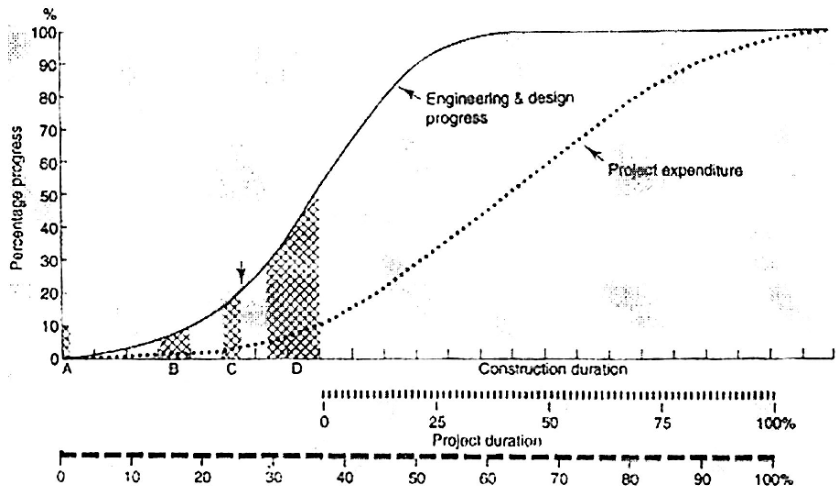


Figure 19.C.10. Time phasing of estimates.

These companies develop the estimates and use them during the course of the installation project as cost control tools for project management.

Phasing of the estimates

The phasing of the estimates in the project schedule is reflected in Figure 19.C.10. The estimates are as follows:

A) Capacity Factored
B) Machinery and Equipment
C) Semi Definitive
D) Definitive

Crude oil

Crude oil is a mixture of hydrocarbon compounds. These compounds range in boiling points and molecular weights from methane as the lightest compound to those whose molecular weight will be in excess of 500. Chapter 1 of this book describes these hydrocarbon families in some detail. Briefly the major groups are:

Paraffins
Olefins
Naphthenes
Aromatics

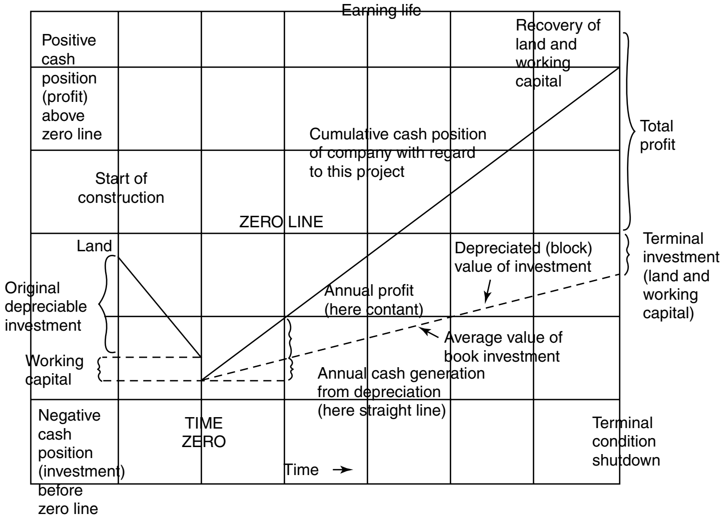


Figure 19.C.11. Graph of cumulative cash flow.

In addition to these basic compounds there will be impurities. The major non-hydrocarbon impurity are the sulfur compounds. In the lighter boiling range of the crude oil sulfur appears mostly in the form of mercaptans, while in the higher boiling point section of the crude the sulfur is in the form of complex thiophenes. In addition to sulfur, nitrogen, and heavy metal are usually present in small quantities, but are sufficient to cause problems to some processes. Olefins are usually present in small quantities in the crude oil, but are produced in the processes of refining the crude. Most notably are the thermal and fluid catalytic process that produce olefins.

The nature and the properties of crude oil vary considerably. This variation is usually connected to the area from which the crude oil is produced. The properties of crude oils from respective sources are recorded in the Crude Assay which is produced by the vendors of the individual crude oils.

Summary assays of the more common crude oils are produced as Appendix 3 to this part of the book.

Cumulative cash flow and present worth

There are several methods of assessing profitability based on discounted cash flow (DCF), but the most reliable yard stick is a return on investment method using the Present Worth (or Net Present Value) concept. This concept equates the present value of a future cash flow as a product of the present interest value factor and the future cash flow. *Based on this concept, the Return on Investment is that Interest value or*

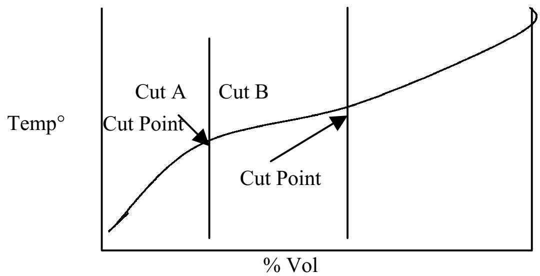


Figure 19.C.12. Typical cut points on a TBP curve.

Discount Factor which forces the Cumulative Present Worth value to Zero over the economic life of the project.

The calculation itself is in two parts, which are:

- Calculation of Cash Flow
- Present Worth Calculation

Both these calculations are described in detail in Chapter 17 of this book. The phases and summary of Cumulated Cash Flow is provided by Figure 19.C.11.

The calculation for present worth is iterative, and is fully explained in Chapter 17 with an example calculation.

Cut points

A cut point is defined as that temperature on the whole crude TBP curve that represents the limits (upper and lower) of a fraction to be produced. Consider the curve shown in Figure 19.C.12. Below of a typical Crude oil TBP curve.

A fraction with an upper cut point of 100°F produces a yield of 20 vol% of the whole crude as that fraction. The next adjacent fraction has a lower cut point of 100°F and an upper one of 200°F this represents a yield of 50–20% = 30 vol% on crude.

D

De-aromatization process

The de-aromatization process is a hydrotreating process that converts aromatic compounds to naphthenes and paraffins. Its most common use is to lower the smoke

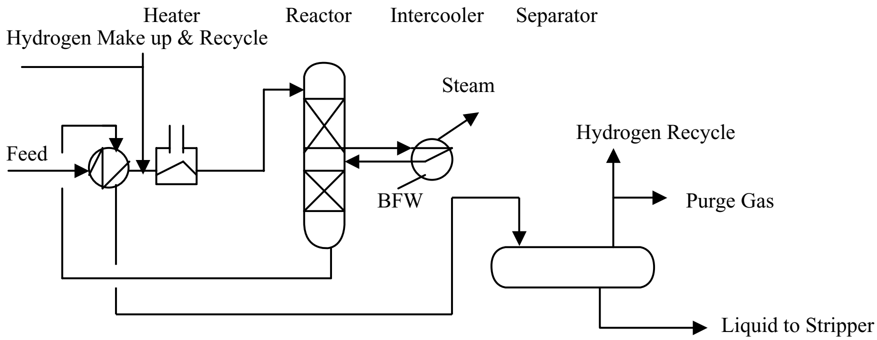


Figure 19.D.1. Typical hydro de-aromatizer process.

point of kerosene, particularly if the product is to be blended to make aviation turbine gasoline. Initially the reduction of kerosene smoke point was effected by the removal of aromatic compounds by extraction using liquid SO_2. A typical kerosene de-aromatizing unit is shown as Figure 19.D.1.

De-sulfurized kerosene feed is introduced and preheated with hot reactor effluent. Hydrogen make-up and the hydrogen recycle stream are mixed with the preheated feed to enter the reactor heater which rises the feed temperature to reaction temperature. Leaving the heater the feed enters the top catalyst bed of the reactor. It flows down through the bed consisting of a nickel type catalyst. The reaction is exothermal and temperature is controlled by an inter-cooler between the top bed and a second catalyst bed. Steam is generated in the inter-cooler as the cooling medium. The reactor effluent leaves the second catalyst bed to be condensed by heat exchange with incoming feed, and, if necessary, by a trim air cooler. This condensate enters a separator drum the pressure of which is set to remove a light hydrocarbon and hydrogen stream at a temperature of 100°F. The pressure in this drum also determines the reactor pressure and, depending on the catalyst used, will be between 350 and 450 psig. The liquid from the separator will be stripped free of light ends in a conventional trayed and reboiled stripper column. The purity of the hydrogen recycle stream is maintained by removing a purge stream that reduces the total hydrocarbons in the recycle. The recovery of kerosene product by this process is between 85% and 90% volume.

De-asphalting process

De-asphalting the heavy end of crude, that is the vacuum residue, is not entirely reserved for the production of lube oils. In energy refineries it is used to remove the asphaltene portion of the residue to prepare a suitable feedstock for catalytic conversion units. In most of these conversion units the performance of the catalyst is greatly

impaired by the presence of heavy metals and the high Conradson carbon content of the residue feed. Most of the metals are entrained in the asphaltene compounds which make up most of the asphalt portion of the residue. These asphaltenes are also high in Conradson carbon content, so the removal of these serves to eliminate both the heavy metal content and the high Conradson Carbon. In the case of lube oil production, the light liquid phase resulting from the extraction of the asphalt makes excellent lube base oil. This de-asphalted oil is termed 'Bright Stock' and can now be further refined in the same way as neutral base stock, which are vacuum distillates, to meet the specifications for blend stocks. Details of the process are given in Chapter 12 of this book.

De-butanizer

De-butanizers are used in refineries to remove butanes and lighter compounds from product streams. The most notable of the feed streams is the overhead distillate from the atmospheric crude distillation tower. Other uses of this process are in the removal of these light ends from hydrotreaters (kero & heavier products), and the reactor effluent liquids from catalytic reforming and hydrocracking. The overhead from the fluid catalytic cracker main tower is also debutanized, but the butane compounds from this process will also contain the olefinic compounds from the cracking process. A typical process configuration for a debutanizer is shown below as Figure 19.D.2.

The debutanizer operates at an overhead accumulator pressure of about 125 psia at 100°F. Usually the whole column overhead is condensed under these conditions

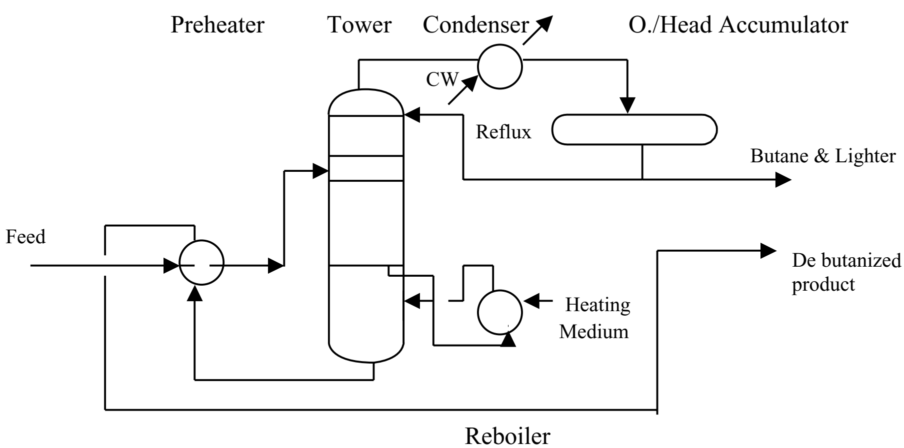


Figure 19.D.2. A typical de-butanizer configuration.

unless there is hydrogen present. Thus, in the case of hydotreaters, reformers, and hydrocrackers there will be partial condensation and there will be a vapor phase from the drum as well as the liquid distillate. The tower will consist of between 30 and 35 distillation trays and the external reflux will be about 2 : 1. More details and design procedures are given in Chapter 4 of this Handbook.

De-ethanizer

The purpose of the de-ethanizer is to remove ethane from the product stream of LPG. Normally it will be the last tower in a light end distillation configuration (see the item 'Light End Distillation' under 'Distillation' in this Part 2 of the book. The de-ethanizer tower operates at an overhead accumulator of below 450 psia at 100°F. This ensures that the operating pressure at the bottom of the tower, which is propane LPG, will be below its critical pressure. In the design example given in Chapter 4 the pressure in the accumulator was calculated to be 350 psia at 100°F, and this was the dew point of the overhead vapor product. De-ethanizers operating without overhead refrigeration facilities have partial condensers and in this case only sufficient overheads from the tower are condensed to meet the reflux required in the tower. Thus the accumulator becomes a theoretical tray itself and there will be no liquid distillate product as such.

De-propanizer

In the refinery configuration of light ends distillation this unit is usually located between the de-butanizer and the de-ethanizer. The process flow is similar to the de-butanizer, with total overhead product and reflux being condensed. The tower operates at a reflux drum pressure of between 200 and 250 psia at 100°F. The tower contains 35–40 actual trays, and the bottom product will be butane LPG. The overhead distillate will be feed to the de-ethanizer whose bottom product will be propane LPG.

Dew points

Is the temperature and pressure condition at which a hydrocarbon vapor begins to condense. That is in a calculation the sum of the mole fraction composition of the vapor divided by the equilibrium constant of each compound must equal the sum of the sum of the mole fraction of the liquid phase at the dew point condition of temperature and pressure. The following example illustrates this concept. (This example is based on a tower top condition for an atmospheric crude distillation unit.)

The following dew point calculation will be carried out at 8.3 psia which is the partial pressure of the hydrocarbons in the overhead vapor.

		1st Trial @ 220		2nd Trial @ 225°F						
COMP	Mole Frac *Y*	*K*	$X = Y/K$	*K*	$X = Y/K$	MOL wt	Weight factor	SG	Vol factor	Liquid prop
C_2	0.008	–	NEG		NEG					
C_3	0.054	84.3	0.001	93.9	0.001	44	0.044	0.508	0.009	
iC_4	0.021	38.6	0.001	39.8	0.001	58	0.058	0.563	0.010	Mol wt = 130.7
nC_4	0.084	29.52	0.003	30.1	0.003	58	0.174	0.584	0.030	
C_5	0.143	12.53	0.011	12.65	0.011	72	0.792	0.629	0.126	SG = 0.766
C_6	0.155	4.70	0.033	4.94	0.031	85	2.635	0.675	0.390	
C_7	0.175	2.17	0.081	2.19	0.080	100	8.00	0.721	1.110	°API = 53
Mid-BP 260	0.124	1.00	0.124	1.16	0.107	114	12.198	0.743	1.642	
Mid-BP 300	0.124	0.506	0.245	0.518	0.239	126	30.114	0.765	3.936	K = 12
Mid-BP 340	0.075	0.229	0.328	0.253	0.293	136	39.848	0.776	5.135	
Mid-BP 382	0.037	0.108	0.343	0.126	0.294	152	44.688	0.788	5.671	
Totals	1.000		1.170		1.06	130.7	138.551	0.767	18.059	

$$K = \frac{\text{Vapor press @ selected temperature}}{\text{Total systems pressure}}$$

$$\text{2nd trial} = 0.108 \times 1.170 \text{ (`}K\text{' for mid-BP 362 component)}$$

$$\text{New K} = 0.126 \text{ then VP} = 8.3 \text{ psia} \times 0.126 = 1.05 \text{ psia} \equiv 225°\text{F}$$

2nd trial is close enough to $\sum x_i = 1.00$

Notes:

a. In estimating for the 2nd trial and final temperature the '*K*' of the highest *X* component is multiplied by the total value of *X* function. Then vapor pressure curves are used to give the component temperature corresponding to this new vapor pressure.

b. The molar composition of the final '*X*' is the composition of the liquid in equilibrium with the product vapor.
The tower top conditions are 229°F @ 15 psig. (This is total pressure and includes the steam effect)

Diesel oil

Diesel oil (sometimes called automotive gas oil) is used as fuel for heavy internal combustion engines such as heavy lorries and rail locomotives. Its main component is the light gas oil cut from the atmospheric crude distillation unit. This product has

Table 19.D.1. A shortened diesel fuel specification

				Method of Test
Specific gravity @ 60°F			0.820–0.860	ASTM D 1298
Color NPA			3 Max	ASTM D 155
Pour point	Summer	°F	15	ASTM D 97
	Winter	°F	7	
Cloud point	Summer	°F	N/A	ASTM D 97
	Winter	°F	N/A	
Sulfur % wt			0.1	ASTM D 129
Diesel index			54 Min	IP 21
Cetane number			47 Min	ASTM D 613
Distillation:				
Recovered at 230°C		% Vol	10 Min	ASTM D 158
" 240°C		% Vol	50 Max	
" 347°C		% Vol	50 Min	
" 370°C		% Vol	95 Max	
FBP		°C	385 Max	
Flash point (PM)		°F	14 0 Min	ASTM D 93

a boiling range of around 480°–610°F. This cut is hydrotreated to remove sulfur (and the process does reduce pour and cloud points to some extent), and blended with kerosene and some heavier middle distillate stock to meet the diesel oil specification. A summarized specification is given below as Table 19.D.1.

Because diesel oil is a motive fuel and therefore emissions are in direct contact with the general public, extensive emission controls are in place. These include the composition of the fuel itself and the engine design in which it is used. Full details of these controls are described and discussed in Chapters 2 and 16 of this book.

Distillate hydro cracking

Hydrocracking is a versatile catalytic refining process that upgrades petroleum feedstocks by adding hydrogen, removing impurities, and cracking to a desired boiling range. Hydrocracking requires the conversion of a variety of types of molecules and is characterized by the fact that the products are of significantly lower molecular weight than the feed. Hydrocracking feeds can range from heavy vacuum gas oils and coker gas oils to atmospheric gas oils. Products usually range from heavy diesel to light naphtha.

While the first commercial installation of a unit employing the type of technology in use today was started up in Chevron's Richmond, California, refinery in 1960, hydrocracking is one of the oldest hydrocarbon conversion processes. Hydrocracking technology for coal conversion was developed in Germany as early as 1915 designed to secure a supply of liquid fuels derived from domestic deposits of coal. The first

plant for hydrogenation of brown coal was put on stream in Leuna, Germany, in 1927, applying what may be considered the first commercial hydrocracking process.

In the mid-1950s the automobile industry started the manufacture of high-performance cars with high-compression ratio engines that required high-octane gasoline. Thus catalytic cracking expanded rapidly and generated, in addition to gasoline, large quantities of refractory cycle stock that was a material that was difficult to convert to gasoline and lighter products. This need to convert refractory stock to quality gasoline was filled by hydrocracking. Furthermore, the switch of railroads from steam to diesel engines after World War II and the introduction of commercial jet aircraft in the late 1950s increased the demand for diesel fuel and jet fuel. The flexibility of the newly developed hydrocracking processes made possible the production of such fuels from heavier feedstocks. The early hydrocrackers used amorphous silica alumina catalysts. The rapid growth of hydrocracking in the 1960s was accompanied by the development of new, zeolite based hydrocracking catalysts. They showed a significant improvement in certain performance characteristics as compared with amorphous catalysts: higher activity, better ammonia tolerance, and higher gasoline selectivity.

There are several process flow schemes for the Hydrocracker process. These are discussed in Chapter 7. The following recycle flow scheme is one of the more common flow configuration (Figure 19.D.3).

Hydrocracking reactions proceed through a bifunctional mechanism. A bifunctional mechanism is one that requires two distinct types of catalytic sites to catalyze separate steps in the reaction sequence. These two functions are the acid function, which

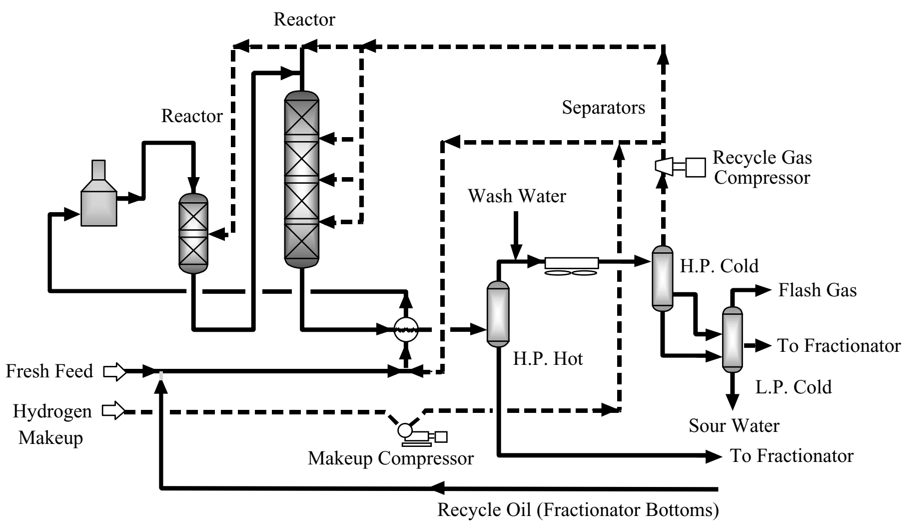
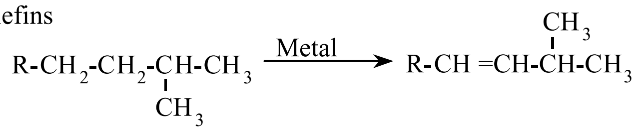


Figure 19.D.3. A distillate hydrocracker reactor section.

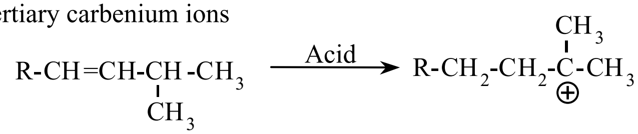
provide for the cracking and isomerization and the metal function, which provide for the olefin formation and hydrogenation. The cracking reaction requires heat while the hydrogenation reaction generates heat. Overall, there is heat release in hydrocracking, and just like in treating, it is a function of the hydrogen consumption (the higher the consumption, the more important the exotherm). Generally, the hydrogen consumption in hydrocracking (including the pre-treating section) is 1,200–2,400 SCFB/wt% change (200–420 Nm^3/m^3/wt% change) resulting in a typical heat release of 50–100 Btu/Scf H_2 (2.1–4.2 kcal/m^3 H_2) which translates into a temperature increase of about 0.065°F/Scf H_2 consumed (0.006°C/Nm^3/m^3 H_2). This includes the heat release generated in the treating section. In general, the hydrocracking reaction starts with the generation of an olefin or cycleolefin on a metal site on the catalyst. Next, an acid site adds a proton to the olefin or cyclo-olefin to produce a carbenium ion. The carbenium ion cracks to a smaller carbenium ion and a smaller olefin. These products are the primary hydrocracking products. These primary products can react further to produce still smaller secondary hydrocracking products. Some of these reactions are given in Figure 19.D.4.

Full details and discussion on Flow schemes and hydrocracking reactions are given in Chapter 7.

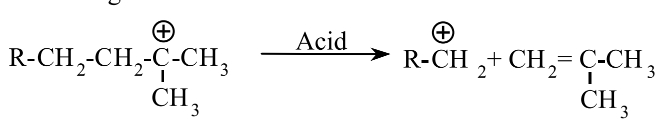
(A) Formation of olefins



(B) Formation of tertiary carbenium ions



(C) Isomerization and cracking



(D) Olefin hydrogenation

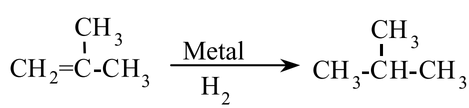


Figure 19.D.4. Hydrocracking reactions of paraffins.

Distillation

Part 1: Laboratory distillation tests

- *The ASTM distillation curve.* While the TBP curve is not produced on a routine basis the ASTM distillation curves are. Rarely however is an ASTM curve conducted on the whole crude. This type of distillation curve is used however on a routine basis for plant and product quality control. This test is carried out on crude oil fractions using a simple apparatus designed to boil the test liquid and to condense the vapors as they are produced. Vapor temperatures are noted as the distillation proceeds and are plotted against the distillate recovered. Because only one equilibrium stage is used and no reflux is returned, the separation of components is poor and mixtures are distilled. Thus the initial boiling point for ASTM is higher than the corresponding TBP point and the final boiling point of the ASTM is lower than that for the TBP curve. There is a correlation between the ASTM and the TBP curve, and this is dealt with later in Chapter 1 of this Handbook.
- *The true boiling point curve (TBP).* This is a plot of the boiling points of almost pure components, contained in the crude oil or fractions of the crude oil. In earlier times this curve was produced in the laboratory using complex batch distillation apparatus of a hundred or more equilibrium stages and a very high reflux ratio. Nowadays this curve is produced by mass spectrometry techniques much quicker and more accurate than by batch distillation.
- *The equilibrium vaporization curve (EFV).* The EFV curve of an oil is determined in a laboratory using an apparatus that confines liquid and vapor together until the required degree of vaporization is achieved. The percentage vaporized is plotted against temperature for several runs to produce the EFV curve. Separation is poorer for this type of distillation than for an ASTM or TBP. Therefore the initial boiling point will be higher for the EFV than for the ASTM. The final boiling point of the EFV will be lower than that for the ASTM. This test is rarely done but the EFV curve is calculated either from a TBP curve or an ASTM curve. These methods are given in Chapters 1 and 3.

Part 2: The distillation processes

Next to heat exchange the unit operation of distillation is the most utilized operation in oil refining. The separation of products by distillation fall into three major categories. These are:

- Total vapor condensation such as the atmospheric crude distillation
- Vacuum distillation processes. Such as the vacuum distillation of atmospheric residue
- Light ends distillation

- *Total vapor condensation processes.* The best example of this type of distillation units in modern refining is the atmospheric crude distillation unit. In these type of units the feed is heated and vaporized to a temperature above the total product cut point. This mixed vapor/liquid is produced by an external heater (and heat exchanger system) and the mixed stream flashed in the lower section of a tower. The vapor rises in the tower and condensed by cooled reflux stream at various stages up the tower according to the various distillate boiling points. Full details of this type of distillation is given in Chapter 3 of this book. Similar distillation systems are also used in the primary separation of Fluid Catalytic Cracking Unit effluent, and the reactor effluent from hydrocrackers.
- *Vacuum distillation processes.* These processes are designed to operate as total vapor condensation similar to the atmospheric units. However the feed to these units is usually heavy residual oils, which if heated to vaporize the product distillate required at atmospheric pressure (or near atmospheric pressure) would cause the feed to crack and coke. The system is therefore set at low vacuum pressure so that the vaporizing temperature is well below the feed's cracking properties. The distillates are produced in the same way as that for the atmospheric units. That is by selective cooled reflux streams. Full details of a crude oil vacuum process are also given in Chapter 3 of this book. Vacuum distillation is also used for the distillation of light residues from hydrocrackers to produce light vacuum distillates and heavy residuum for further thermal cracking.
- *Light ends distillation.* The most common of this type of distillation is the crude unit light ends process. The feed to this unit is the overhead distillate from the atmospheric crude unit. This feed may also include overhead distillate from other processes (such as the catalytic reformer). The product from the light end s process is the production of light and heavy naphtha, butane LPG, propane LPG, and refinery gas. These processes are discussed fully in Chapter 4 of this book.

Drums

Drums may be horizontal or vertical vessels. Generally drums do not contain complex internals such as fractionating trays or packing as in the case of towers. They are used however for removing material from a bulk material stream and often use simple baffle plates or wire mesh to maximize efficiency in achieving this. Drums are used in a process principally for:

- Removing liquid droplets from a gas stream (knockout pot), or separating vapor and liquid streams
- Separating a light from a heavy liquid stream (separators)
- Surge drums to provide suitable liquid hold up time within a process
- To reduce pulsation in the case of reciprocating compressors

Drums are also used as small intermediate storage vessels in a process.

Vapor disengaging drums

One of the most common example of the use of a drum for the disengaging of vapor from a liquid stream is the steam drum of a boiler or a waste heat steam generator. Here the water is circulated through a heater where it is risen to its boiling point temperature and then routed to a disengaging drum. Steam is flashed off in this drum to be separated from the liquid by its superficial velocity across the area above the water level in the drum. The steam is then routed to a super-heater and thus to the steam main. The performance of the steam super-heater depends on receiving fairly "dry" saturated steam. That is steam containing little or no water droplets. The separation mechanism of the steam drum is therefore critical.

The design of a vapor disengaging drum depends on the velocity of the vapor and the area of disengagement. This is expressed by the equation:

$$V_e = 0.157\sqrt{\frac{\rho_l - \rho_v}{\rho_v}}$$

where

V_c = Critical velocity of vapor in ft/sec.
ρ_l = Density of liquid phase in lbs/cuft.
ρ_v = Density of vapor phase in lbs/cuft.

The area used for calculating the linear velocity of the vapor is:

- The vertical cross sectional area above the high liquid level in a horizontal drum
- The horizontal area of the drum in the case of vertical drums

The allowable vapor velocity may exceed the critical, and normally design velocities will vary between 80% and 170% of critical. The use of crinkled wire mesh screens (CWMS) screens are an effective entrainment separators and are often used in separator drums for that purpose.

Liquid separation drums

The design of a drum to perform this duty is based on one of the following laws of settling:

Stoke's law

$$V = 8.3 \times 10^5 \times \frac{d^2\,\Delta S}{\mu}$$

When the Re number is < 2.0.

Intermediate law

$$V = 1.04 \times 10^4 \times \frac{d^{1.14} \Delta S^{0.71}}{S_c^{0.29} \times \mu}$$

When the Re number is 2–500.

Newton's law

$$V = 2.05 \times 10^3 \times \left[\frac{d \cdot \Delta S}{S_c}\right]^{1/2}$$

When the Re number is > 500,

where

$$\text{Re number} = \frac{10.7 \times d_v S_c}{\mu}$$

V = Settling rate in ins per minute.
d = Droplet diameter in ins.
S = Droplet specific gravity.
S_c = Continuous phase specific gravity.
ΔS = Specific gravity differential between the two phases.
μ = Viscosity of the continuous phase in cps.

The following may be used as a guide to estimating droplet size:

Lighter Phase.	*Heavy Phase.*	*Minimum Droplet Size.*
0.850 SG and lighter.	water	0.008 ins.
Heavier than 0.850.	water	0.005 ins.

The holdup time required for settling is the vertical distance in the drum allocated to settling divided by the settling rate.

Settling baffles, are often used to reduce the holdup time and the height of the liquid level.

Surge drums

This type of drum, the calculation of holdup time and surge control is used in the control the movement of liquids from one process to another. It's purpose is to smooth out the flow to meet the process criteria. For example, when a liquid feed leaves the first process item (such as an overhead reflux drum) under level control a surge drum may be used to collect the feed and deliver it under flow control to the next process. This is particularly desirable if the feed enters a fired heater as the first item of the second process.

Pulsation drums or pots

This type of drum is used almost entirely in the operation of a reciprocating compressors. It is used to smooth out the compressed gas flow leaving the compressor cylinders.

E

Economic evaluations

Economic evaluation is used for most aspects of the refinery planning, and its operation. The methods used in this evaluation may differ from company to company, but the end product must reflect the profitability of the present and often the future profitability of a proposed venture or operation. This measure is reflected in terms of the Return on Investment of the item. This is described and discussed in Chapter 8.

The following definitions and items are used in the economic evaluation exercises:

Ad volorum tax. This is the fixed tax levied in most countries payable to local municipal authorities, provincial, or state authorities to cover property tax, municipal service costs etc.

Calculation of cash flow method. There are several methods of assessing profitability based on discounted cash flow (DCF), but the most reliable yardstick is a return on investment method using the Present Worth (or Net Present Value) concept. This concept equates the present value of a future cash flow as a product of the present interest value factor and the future cash flow. *Based on this concept, the Return on Investment is that Interest value or Discount Factor which forces the Cumulative Present Worth value to Zero over the economic life of the project.*

Net investment costs. The Net Investment for the project includes the capital cost of the plant, which is subject to depreciation, and the Associated Costs, which may not be subject to depreciation.

The capital cost of the plant is the contractor's selling price for the engineering, equipment, materials, and the construction of the facilities. In a process study using a DCF return on investment calculation, the capital cost should be an estimate with an accuracy at least that based on an equipment factored type.

The associated costs include the following elements:

- Any licensor's paid up royalties
- Cost of land
- First inventory of chemicals and catalyst
- Cost of any additional utilities or offsite facilities incurred by the project
- Change in feed and product inventory
- Working capital

Capitalized construction period loan interest

Construction period. This is the period before year 0 during which the plant is constructed and commissioned. Assume this period is 3 years, this is designated as end of year –2, –1, 0. During this period, the construction company will receive incremental payments of the total capital cost of the plant with final payment at the end of year 0. The construction cost may be paid from the company's equity alone or from equity and an agreed loan or entirely from a loan. In the case of a loan to satisfy this debt, the payment of the loan interest commences in this period. The interest payment over this period, however, is usually capitalized and paid over the economic life of the project.

Depreciation. Part of the cost to a project or venture which is considered as a deductible from the gross profit for tax purposes is the depreciation of the plant value. This is calculated over the PLANT LIFE as the plant capital cost divided by the plant life. The term Plant Life is the predicted life of the facility before it has to be dismantled and sold for scrap. Usually this is set at 20 years and indeed all specifications relating to engineering and design of the facilities will carry this requirement. So all material and design criteria, such as corrosion allowances, associated with the plant will meet this plant life parameter.

Discounted cash flow, definition of. The development of a DCF return on investment is a combined effort between the Technical Disciplines and the company's Finance Specialist. The engineers provide the technical input to the work such as operating costs, type of plants, construction schedules, and cost, yield and refinery fence product prices, and the like. While the financial specialist provides the financial data based on statutory and company policies, such as the form of depreciation, tax exemptions, tax credits (if any), items forming part of the company's financial strategy, etc. The calculation itself is in two parts, which are:

- Calculation of Cash Flow
- Present Worth Calculation. (or any other method for calculating the Return on Investment the Company may use)

Economic life. This is the number of years over which the project is expected to yield the projected profit and pay for its installation. These are the number of years

starting at year 0 which indicates the end of construction and the commissioning of the facilities. The last year (usually year 10) is the year in which all loans and other project costs are repaid and the "Terminal Investment" released.

Plant Operating Cost. This includes the cost of utilities used in the process, such as power, steam, and fuel. It also includes the cost of plant personnel in salaries, burdens, and indirects and the cost of chemicals and catalyst used.

- *Maintenance.* There are two kinds of maintenance costs included in this item These are the preventive maintenance carried out on a routine basis, and those costs associated with incidental breakdowns and repair.
- *Loan repayment.* The loan principal is paid back in equal increments over the economic life of the plant. This item includes the payback increments and the associated interest on a declining basis.

Net cash flow. This item is calculated for each year of the project's economic life. It commences with year 0 with the net investment shown as a negative net cash flow item. Then for each successive year until the end of the last year of the economic life, the net cash flow is calculated as the sum of Profit After Tax *PLUS* Depreciation.

The depreciation is added here because it is not really a cost to the project. It is a "Book" cost only and is used specifically for tax calculation.

The cash flow item for the last year of the economic life must now include the "Terminal Investment Item". This item is the sum of the net scrap value of the plant (scrap value less cost of dismantling), the estimated value of the land and the Working Capital initially used as part of the "Associated Costs".

Thus, the final cash flow item will be the sum of Profit After Tax, plus Depreciation, plus Terminal Investment.

With the Net Cash Flow in place, the second part of the calculation which is the determination of the Return on Investment for the project can be carried out.

Pay out time. The pay out time for a project or any venture is given by the expression:

$$\frac{\text{Net Investment Cost}}{\text{Net Income after taxes} + \text{depreciation}} = \text{Years}$$

Simple return on investment. This calculation is used for screening purposes of several options that are apparent in any venture. It does not consider construction time or the

discounting of the cash flow over the economic life of a plant. Its definition is given by the equation:

$$\frac{\text{Net Income after Taxes}}{\text{Net Investment Cost}} \times 100 = \%\ \text{ROI}$$

Where

Net Investment is Capital Cost plus Associated Cost.
Net Income is Gross income less operating cost, depreciation, and tax.

Revenue. This is income received for the sale of the product(s). This is calculated from projected process yields of products multiplied by the market price of the products. A market survey should already have been completed to ensure that the additional products generated by the project are in demand and the price is in an acceptable range. Later, a sensitivity analysis of the DCF return on investment may be conducted changing the revenue recovered by price escalation or other means.

Taxable income. Taxable income is revenue less operating cost, depreciation, and Ad Valorem Tax. This of course is simply put as in most countries, states, or provinces there will probably be certain local tax relief principals and tax credits that will affect the final taxable income figure. The company's financial specialist will be in the position to apply these where necessary.

Tax. This is quite simply the tax rate applied to the "Taxable Income" figure. This will vary from location to location but will be taken as one rate over the economic life of the project for the purpose of a process study, unless there are legislative changes already in place.

Working capital. In all capital projects there is initially a financial loss when the company has to purchase land, equipment, pay contractors to erect equipment, and the like. To do this not unlike most private individuals, companies may need to borrow money, on which of coarse they have to pay interest. In addition to the cost of construction, the company must keep in hand some capital by which it can buy feedstock, chemicals, and pay the salary of its staff during the commissioning and the initial operation of the plant. During this initial operation, the working capital must also be considered as debt. At the end of this period of the project initiation, the operation must recover the working capital and make its prescribed profit.

Edmister correlations

A series of correlations which relates an ASTM distillation test to the TBP of a petroleum cut is presented in W. Edmister's publication titled "*Applied*

Thermodynamics". The correlation relating to the ASTM and TBP curves from this book is used in this Handbook and is given in Chapter 1. Similar correlations have also been prepared by Edmister for the relation between TBP and the equilibrium flash vapor curve (EFV).

Effluent water

This item is described and discussed in Chapter 14. Pollutants in waterways from refineries are listed in the following table.

Process	Waste water	Air
Atmospheric and vacuum distillation	Sour water (NH_3 & H_2S) Desalter water Spent caustic Process area waste water (pump glands, area drains etc)	Furnace Flue gases—SO_2
Thermal cracking	Sour water	Furnace
Delayed coking	Decking water (Oil) Process area waste water	Flue gases
Fluid cat cracking	Sour water (NH_3, H_2S, Phenols)	Furnace
Unsat gas plant	Spent caustic Process area waste water.	Flue gases SO_2, CO particulates.
Hydrocracker hydrogen plant	Sour water (inc Phenols) Process area waste water	Furnace Flue gases SO_2
Sat gas plant alkylation	Spent caustic Process area waste water	Nil
Naphtha hydrotreater Cat reformer	Sour water Process area waste water	Furnace Flue gases
Sulfur plant	Nil	Incinerator Flue gas—SO_2 Hydrocarbons—Flare
Tankage area	Tank dike area drains Non contaminated rain runoff	Tank vents Hydrocarbons.

The most undesirable pollutants in aqueous waste streams are:

- Those that deplete the dissolved oxygen content of the waterways into which they discharge.
- Those contaminants that are toxic to all forms of life, such as arsenic, cyanide, mercury, and the like.
- Those contaminants that impart undesirable tastes and odors to streams and other waterways into which they discharge.

Oxygen depletion occurs by the introduction of one or more of the following oxidizable contaminants entering the waterway:

- Natural pollution by surface run-off rainwater, or melting snow, in the form of soluble salts leached from the earth.
- Natural pollution caused by decay of organic plants from swamps or other sources.
- Human and animal life excretion.
- Chemical pollution from reducing agents in industrial plant wastes. Such as sulfides, nitrites, ferrous salts, etc.
- Biochemical pollution from such industrial wastes as phenols, hydrocarbons, carbohydrates, and the like.

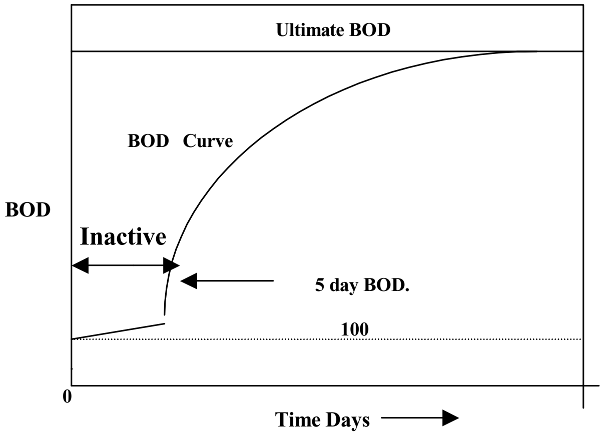
The degree of oxygen depletion from the pollution sources described above may be catalogued by the following terms:

BOD—Biological Oxygen Demand
COD—Chemical Oxygen Demand
IOD—Immediate Oxygen Demand

BOD. Since all natural waterways will contain bacteria and nutrients; almost any waste compound introduced into the waterways will initiate biochemical reactions. These reactions will consume some of the dissolved oxygen in the water.

The depletion of oxygen due to biological pollution is not very rapid. It follows the laws of first order reaction. Because of this, the effect of BOD is measured in the laboratory on a five day basis, and has been universally adopted as the measure of pollution effect. The "Ultimate" BOD is a measure of the total oxygen consumed when the biological reaction proceeds to almost completion. The "5 day" BOD is believed to be approximately the Ultimate.

In summary, BOD measures organic wastes which are biologically oxidizable.



COD. The COD is a measure of the oxygen depletion due to organic and inorganic wastes which are chemically oxidizable. There are several laboratory methods accepted to measure the oxygen depletion effect of these pollution. The two most widely accepted are the "4 hour Permanganate" method or the "2 hour Dichromate" method. Although there is no generalized correlation between BOD and COD, usually the COD will be larger than the BOD. The following table illustrates how different wastes exhibit a different relationship between COD and BOD.

Source	Pollutants	BOD "5 day"	COD "2 hr dichromate"
Brewery	Carbohydrates Proteins	550	–
Coal gas	Phenols, Cyanides Thiocyanates Thio sulphates	6,500	16,400
Laundry	Carbohydrates Soaps	1,600	2,700
Pulp mill	Carbohydrates Lignins, Sulfates	25,000	76,000
Domestic sewage	Solids, Oil, and Grease, Proteins Carbohydrates	350	300
Petroleum refinery (Sour water)	Phenols Hydrocarbons Sulfides	850	1,500
Petroleum refinery	Phenols, Sulfides Hydrocarbons, Mercaptans, Chlorides	125	2,600

IOD. Oxygen consumption by reducing chemicals such as sulfides and nitrates is typified as follows:

$$S^{--} + 2O_2 \rightarrow SO_4^{--}$$

$$NO_2^- + \tfrac{1}{2}O_2 \rightarrow NO_3^-$$

These types of inorganic oxidation reactions are very rapid and create what is measured in the laboratory as immediate oxygen demand. If waste contaminants contain these inorganic oxidizers, the "5 day" BOD test will include the consumption of the oxygen due to IOD also. A separate test to determine IOD must be made and this result subtracted from the "5 day" BOD to arrive at the true BOD result.

Toxic pollutants common to oil refining. Toxic pollutants that are most commonly contained in untreated refinery aqueous wastes are:

Oil. Heavy oil and other hydrocarbons are the most problematic pollution to be found in refinery water effluent. All refineries exercise the most stringent methods to control and remove these undesirable pollutants. Indeed in many cases the treated effluent streams leaving the refinery may well be purer than incoming portable water used in the processes.

Phenols. This chemical often formed in refinery processes such as catalytic and thermal crackers, are highly toxic to aquatic life in concentrations of 1–10 ppm. Apart from its toxicity phenols also unpleasant taste and odor to drinking water in the range of 50–100 ppb. In concentrations of 200 ppm and more, these chemicals can also deactivate water treatment plants such as trickle filters and activated sludge units.

Caustic soda and derivatives. Solutions containing sodium hydroxide are used in a number of refinery processes. Inevitably some of this chemical enters the refinery's waste water system. This contaminant is toxic to humans and marine life in even low concentrations. The spent caustic (compounds leaving the process) such as sodium sulfide is even more injurious.

Aqueous solutions of ammonium salts. The most common of these are ammonium sulfide NH_4SH, and ammonium chloride. Both these salts are present in effluent water from the crude distillation unit overhead accumulator, however the sulfide salt is present in all aqueous effluents from the cracking processes, and the hydro treaters. Other ammonium salts are also present in hydrocracking and deep oil hydrotreating.

Acids in aqueous effluents. The most common of these are from the alkylation processes which use either hydrofluoric acid or sulfuric acid. In some isomerization processes, hydrochloric acid is used to promote the aluminum chloride catalyst. In some older processes sulfur dioxide is used to remove aromatics. This effluent usually leaves these plants as dilute sulfuric acid.

Ketones, furfural, and urea. These compounds are used in the refining of lube oils. MEK and Urea are used in the dewaxing processes while furfural is used in the extraction processes for finished lube oil stock. All of these compounds are toxic.

Treating refinery aqueous wastes

The treatment of aqueous wastes from oil refineries fall into three categories. These are:

- In-plant treatment. These are onsite processes usually sour water strippers, spent caustic oxidizers, and spent caustic neutralizers.
- The API separator, or similar oil/water separating device.
- Secondary treatment, which includes chemical coagulation, activated sludge processes, trickle filters, air flotation, and aerators.

Most energy refineries contain only the first two of the above categories. These processes are described in detail in this Handbook.

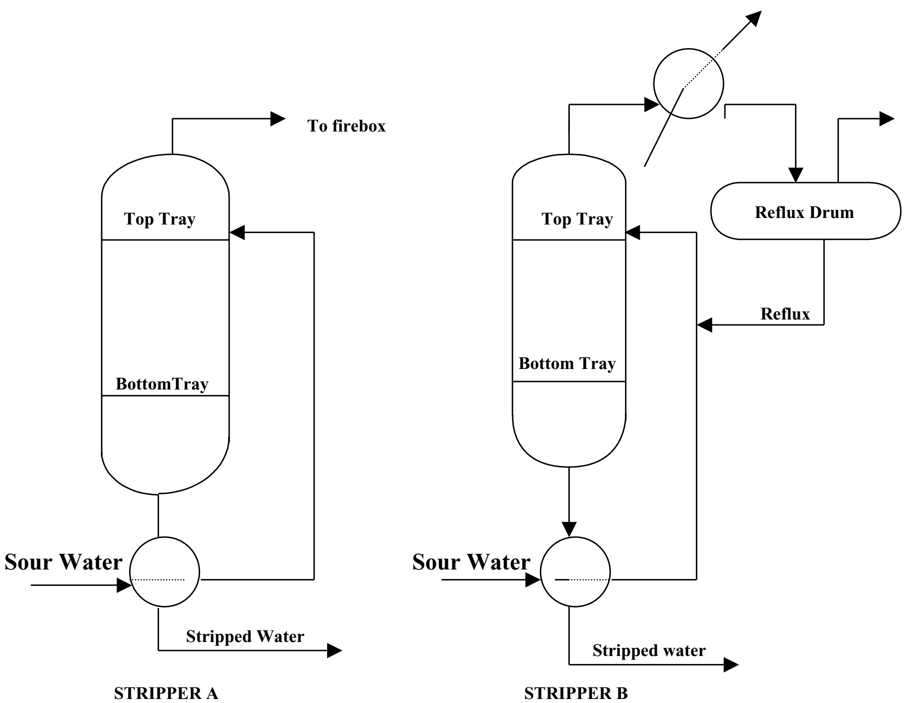
Effluent water treating

Sour water is usually treated in petroleum refineries by one or more of the following processes:

- Steam Stripping
- Caustic/Acid Neutralization
- Caustic Oxidization
- Oil Removal by Settling

All three of these processes with brief description of the more uncommon processes such as coagulation are also described fully in Chapter 14 of this Handbook. A brief summary of these are as follows:

Sour water strippers. This is one of the most common treating processes. Its purpose is to remove the pollutant gases included in process plant effluents. The more common pollutants in this case are ammonia, ammonium salts, and hydrogen sulfide. There are two types of strippers in this service; they are shown as Stripper A and B, respectively, below:



Both these type of sour water stripping lend themselves to tray by tray mass and heat transfer. The sour water feed is introduced on the top tray of the tower while steam usually at a rates of 0.5–1.5 lbs/gallon of feed is introduced below the bottom tray. In the case of a tower with reflux the reflux enters the tower with the fresh feed. The design of both towers utilizes the partial pressure relationship of NH_3 and H_2S in aqueous solution. These relationships are given by a series of graphs to be found in Appendix 1 of Chapter 14.

The sour water stripper is almost always located in the process area of the refinery. The feed to the stripper is the effluent water from the crude unit overhead condenser, the water phase from the desalter, the condensed water from the vacuum unit's hot well, and all the water condensate from the hydro-treater product steam strippers. The sour water stripper may be a single tower with no reflux as in Type A or a single trayed tower with an overhead reflux stream (Type B). The amount of steam used in both cases will be between 0.5 lbs steam per lb of feed to 1.5 lbs of steam.

Spent caustic disposal. The other major effluent from oil refining is the spent caustic streams from hydrogen sulfide removal and also the removal of phenols. Refiners usually have the following options in the disposal of these streams. In order of preference these are listed as follows:

Phenolic spent caustic

- Disposal by sales
- Disposal by dumping at sea
- Neutralizing with acid
- Neutralizing with flue gas

Sulfidic spent caustic

- Disposal by sales
- Oxidation with air and steam
- Neutralization with acid and stripping
- Neutralization with flue gas and stripping

These processes are also described and discussed in full in Chapter 14 of this Handbook. A brief summary is as follows:

Neutralizing phenolic spent caustic. As listed above phenolic spent caustic can be neutralized using acid or flue gas. When neutralized the mixture separates into two liquid phases. The upper phase contains the acid oils while the lower phase is an aqueous solution of sodium sulfate or sodium carbonate. The neutralization using

either acid or flue gas can be accomplished in a batch or continuous operation. The neutralization step is exothermic giving out around 125 Btu/lb of sprung acid. As the objective of the process is to produce a phenol free sprung water for disposal the system temperature should be kept as low as possible until the sprung water is removed. Routing the sprung water to the sour water stripper ensures the removal of any entrained H_2S in that stream.

Spent caustic oxidation. Spent caustic cannot be steam stripped to remove the sulfides contained in it due to the H_2S removal process in which the caustic was used. This is because sodium sulfide does not hydrolyze even when heated. Acids could be used, of course, to neutralize the spent caustic which would release gaseous H_2S. This would however be a costly procedure and causes a potential air pollution problem. The alkaline sulfide can be economically oxidized to form thiosulfates and sulfates. This is the process most commonly used in refineries where only sulfides are the pollutants in the spent caustic and the release of gaseous H_2S is a problem. Details of this process together with a process schematic drawing are given in Chapter 14.

Oil–water separation. Most aqueous effluent from a refinery will contain oil. This oil content has to be reduced to at least 10 ppm before it can be deposited into a river, lake, or ocean. The oil contamination sources are from process water run down, paved area drainage, storm catch-pots, tanker ballast pump out, and tank farm diked areas. All the water from these sources are treated in oil separation processes. The most important of these oil–water separation process is the API Separator.

The API oil–water separator. The design of an API separator is based on the difference in gravity of oil and water in accordance with the general laws of settling. In the design of an API separator a modified version of Stoke's Law is used. In this law the rate of settling is given by the equation:

$$Vr = 6.69 \times 10^4 \frac{d^2 \Delta S}{\eta}$$

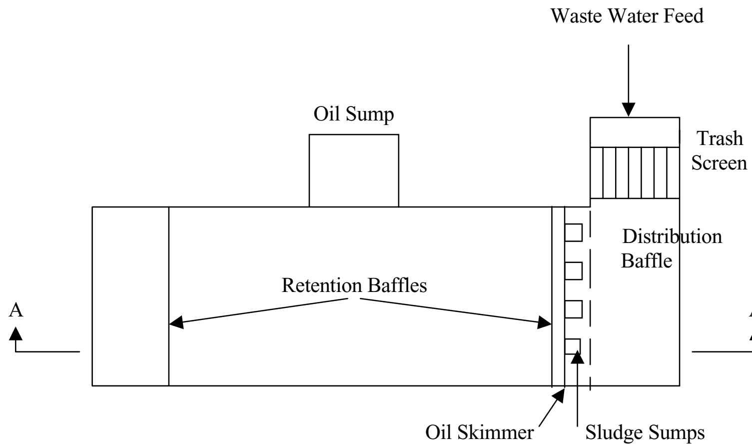
where

Vr = Rising rate of the oil phase in ft/min
d = Droplet diameter in ins.
ΔS = Difference in specific gravity of the phases.
η = Viscosity of the continuous phase (water) in centipoises.

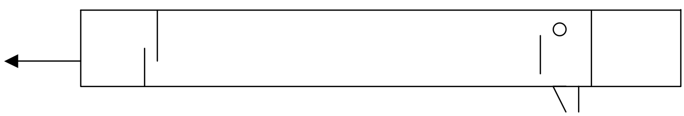
The above modified Stoke's Law for the API separator recognizes that the continuous phase is water and the lighter oil phase is the one that is separated to be disposed as the product skimmed from the surface.

An example of the application of the equation in the design of an API separator is given in Chapter 14 Appendix 14.3 of this Handbook.

The oil phase from the separator is removed using specially designed skim pipes and an oil sump. A simplified diagram of a typical API Separator is given below.



Plan View,



Side View Through A-A

A process description of the separator together with its ancillary equipment is given in Chapter 14.

Storm surge ponds. These ponds are installed to provide storage for maximum rainfall conditions. There are several forms of these surge ponds, some requiring pumps, some located upstream of the API separator, and some downstream of the separator. In most cases, the storm drain system is directed to the storm surge pond. Thus in a storm, the excess rainfall is held in this pond and fed to the API separator, over a period of time and at a rate that will not exceed the separator's capability to handle the water effectively. In this way, the refinery ensures that any oily water will not by-pass the separator under the worst condition. The size of the surge pond must be able to handle

the maximum rainfall and the flow from all catch basins and open culverts that form part of the refinery drainage system.

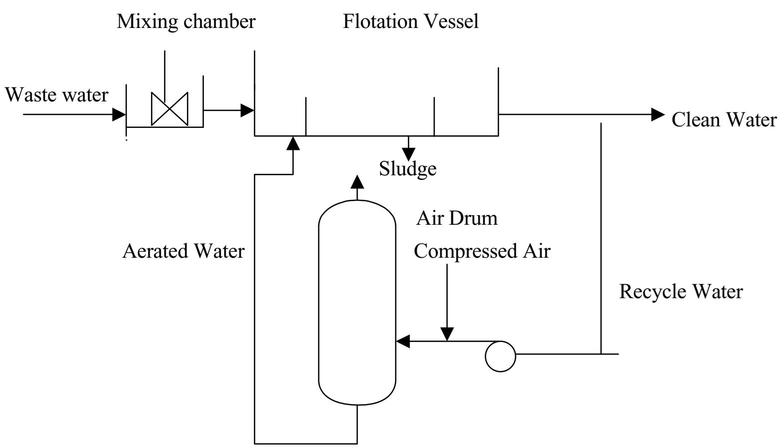
Other refinery water effluent treatment processes. These are summarized below, but are described more fully in Chapter 14.

Oxidation ponds. Oxidation ponds are usually used as a secondary effluent clean up after the API separator. There are three types of these ponds which are:

- Aerobic—Where the oxidation of the water utilizes oxygen from the atmosphere plus oxygen produced by photosynthesis.
- Anaerobic—Where oxidation of the wastes does not utilize oxygen.
- Aerated—Where oxidation of the wastes utilizes oxygen introduced from the atmosphere by mechanical aeration.

The processes described above are those met with in oil refining most often. Indeed of the processes described above most refineries only use the API separator and the surge ponds to meet the oil/water separation required.

Air flotation. The purpose of the air flotation process is the clarification of waste water by the removal of suspended solids and oil. This is achieved by dissolving air in waste water under pressure, and then releasing it at atmospheric pressure. The released air forms bubbles which adhere to the solid matter and oil in the waste water. The bubbles cause the adhered matter to float in the froth on the surface of the water bulk. The dissolved air in the water also achieves a reduction in the BOD of the effluent stream. The figure below shows the principal of a typical air flotation process.

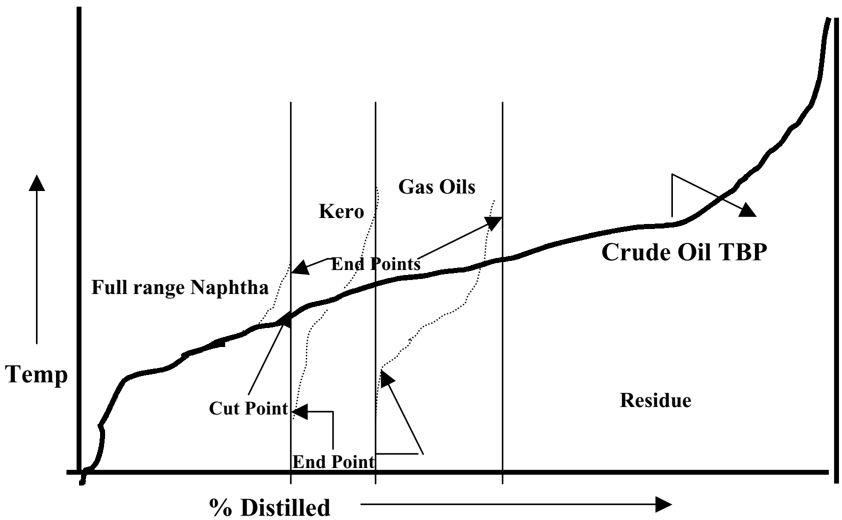


A typical Air Flotation Process

These processes are also described and discussed more fully in Chapter 14.

End points

Whereas a cut point is an ideal temperature on a TBP curve to define the yield of a fraction, the end points define the shape of the fraction when produced commercially. In actual process, the initial boiling point of a fraction will be much lower than its front end cut point. The final fraction boiling point will be higher than the corresponding cut point. This is demonstrated by the figure below:



There is a correlation between the TBP cut point and the ASTM end point. This is described in Chapter 1 of this Handbook. A relationship also exists for the 90% ASTM point and the TBP 90% cut point. With these two ASTM data and using an ASTM probability graph (see Chapter 1) a full ASTM curve with its end points can be drawn. This converted to a TBP curve is used to define the cut's properties.

Engineering flow diagrams

Diagrams are used extensively by all disciplines of engineers to convey ideas and data.

Process engineers use and in some cases develop three types of flow diagrams to project their work and responsibilities.

These are:

- The Process Flow Diagram
- The Mechanical Flow Diagram (sometimes called the P&I Diagram)
- The Utilities Diagram

The process flow diagram is always originated by the process engineer and he retains sole responsibility for its future development and update. The Mechanical flow diagram may also be initiated by the process engineer or it may be developed by others from the process flow diagram. In many companies, however, the process engineer remains responsible for its technical content, development, and its completeness. The utilities diagram shows the routing, sizing, and specification of all the utility flow lines between units and within units of a process. This diagram is usually superimposed on the plot layout diagram. The piping engineers or those engineers who are responsible for initiating the plot plan drawing usually initiate the utilities drawing and administer it. The process engineer in this case is responsible for sizing the flow lines, establishing flow conditions of temperature and pressure, and for ensuring that all lines have been included.

The process flow diagram

This diagram is usually the first drawing that will be produced for an engineering or development project. In some cases, it may be preceded by a process block flow diagram but it is the process flow diagram that is the basis for:

- A process definition
- A budget cost estimate
- An equipment list
- A mechanical flow diagram
- Process equipment data sheets

The flow diagram supports the material and energy balances for the process and establishes the sequence and direction of the process flow. The diagram also shows the control philosophy that will be adopted for the process and the salient temperature/pressure conditions within the process. As a minimum therefore process flow diagrams should contain the following:

Vessels. The outlines of all major vessels, such as towers, drums, tanks are shown. Their equipment item number and their overall dimensions are indicated on the diagram. Where vessels contain special internals, such as trays, demisters, packing, etc these too should be simply indicated on the vessel drawing. For example, the number of trays in a tower may be indicted by showing the top, feed, and bottom trays only but including their respective tray numbers. The main temperature and pressure conditions are also shown on the vessel drawing. For example on fractionation towers the tower top and bottom operating temperatures will be shown but only the top pressure is normally shown.

Heat exchangers. All heat exchangers are shown as single shells on the process flow diagram. That is, no attempt is made to show the number of passes or the type (i.e., shell & tube, or double pipe, etc.) on this diagram. The process flows to and from these

items are shown as flowing through the shell side or the tube side. The exchanger item number only is indicated on the flow diagram adjacent to the equipment drawing. Its equipment name is normally not shown. The heat duty of the exchanger is also shown on the flow diagram again adjacent to the equipment drawing and below the equipment number. The temperature conditions for the exchanger are shown on the process lines in and out of the equipment. No pressures are normally shown for this equipment.

Air coolers. Air coolers are shown simply as a narrow rectangular block in a process line with a fan symbol shown inside the rectangle as a dotted outline. The item number appears directly below the rectangle and below that is given the operating duty of the item in mm Btu/hr or kcal/hr, etc.

Heaters. Fired heaters are shown as box type with a stack outlet. The specific type of heater or the number of tube passes are not shown on the process flow diagram. Again, only the equipment item number and the heater duty is given in the flow diagram adjacent to the item drawing. The heating medium is shown as a single line entering the bottom of the equipment and marked only as 'fuel'. The line would contain a control valve with an instrument control line to the process coil outlet showing the firing control philosophy. The temperatures connected with the heater are shown on the process line in and out of the equipment. Normally no pressure levels are shown for this item.

Pumps. Pumps are shown in as simple a manner as possible. Most companies carry their own symbols for equipment. Many however show a centrifugal pump simply as a circle with the suction line proceeding to the center of the circle and the discharge line leaving tangentially from the top. Other symbols are used for positive displacement pump types. Only these two types are differentiated on the process flow diagram. The various types within these categories are not indicated. The pump item number and an indication as to whether the pump is spared is shown adjacent to the pump drawing on the flow diagram. If the pump is spared then the item number will be followed by "A + B". If it is not spared it will be followed by the letter "A" only. The capacity of the pump as gallons per minute (GPM) or cubic meters per hour will be shown under the item number. This is the normal or operating capacity.

Compressors. These equipment are shown as either centrifugal or reciprocating machines. The centrifugal type are shown similar to the centrifugal pump or as a trapezoid and the reciprocating type is shown as two small square boxes connected by a double line. The item number appears below the item and in some cases indicates the number of stages. The capacity in standard or normal units is given below the item number while the temperature/pressure conditions to and from the item are shown on the process lines to and from.

Process lines. All major process lines interconnecting equipment, recycle, or bypasses are shown on the process flow diagram. These lines will show direction of flow as black arrows on the lines. Control valves and major block valves are also shown on these lines. The temperature and pressure conditions of the flowing material are given on the lines at appropriate positions in the drawing.

Instruments. Only major control instrumentation are shown and the instrument symbols are kept as simple as possible. Details of instrument 'hook ups' are confined to showing the control valve being activated from either a level, flow, pressure, or temperature elements by a dotted line to the valve. The measurement instruments that affect control are shown as circles with the type of instrument (e.g., FC—for flow controller, TC—for temperature controller, etc.) printed in the circle.

The material balance. The material balance for the process represented by the process flow diagram is either shown in table form on the bottom of the flow sheet or on an attached but separate table. Preferably it should appear on the flow sheet itself. The table should contain at least the following:

- The stream number—This is the number given to the process stream and referenced on the respective process line in the diagram. This initiates the columns that will make-up the table.
- The stream identification—This next line should identify the stream, such as "Debutanizer bottoms" for each of the columns.
- The items following down the title column consists of, the flow rate for each stream as wt per unit time, the stream temperature, the specific gravity at a standard temperature for liquids, the mole wt for gas streams, volume flow at standard temperature (and pressure for gasses), stream pressure for gasses.

The mechanical flow diagram

The mechanical flow diagram (MFD) is developed from the process flow diagram. The detail provided by the MFD is sufficient for other engineering disciplines to:

- Initiate a plot layout
- Prepare a line list. (Piping design)
- Initiate piping arrangement drawings (Piping design)
- Prepare a preliminary piping material take off
- Prepare an instrument register (Instrument engineering)
- Initiate instrument "hook up drawings" (Instrument design)
- Prepare electrical "one line drawings" (Electrical engineering)
- Prepare preliminary Instrument and electrical material take off
- Initiate civil and structural design (Civil engineering)
- Develop the project execution plan (Planning engineers)
- Prepare a semi definitive cost estimate (Cost estimators)

To meet these objectives, the Mechanical Flow Diagram will contain more detail of the process and the equipment included in it than the Process Flow Diagram. This is described briefly in the following paragraphs:

Vessels. Vessels are shown in approximate relative size to one another whereever possible. Again, only the top and bottom trays need be shown, unless other trays are required to indicate the location of side draws, instruments, sample points or changes in type of tray layout. Trays are numbered sequentially either from top to bottom or bottom to top. Catalyst beds, packing, demisters, and the type of tray (such as single pass or double pass, etc.) are shown. The height of packing etc is shown adjacent to the vessel and the height of all vessels above grade is also shown on the vessel. The following detail is usually shown on the top of the flow sheet directly above the vessel:

- Vessel Item Number (this should also appear in or near the vessel drawing).
  - ➢ Title
  - ➢ Size (Inside diameter, and length tan to tan)
  - ➢ Design temperature and pressure
  - ➢ Insulation (i.e., Indication is the vessel insulated or not)
  - ➢ Trim Number (Line specification for miscellaneous vessel connections)

Heat exchangers. The actual arrangement and type of heat exchangers are shown on the MFD. Shell and tube exchangers are still shown as circles with tube side flows in dotted lines as in the process flow diagram. Here, however the actual number of shell passes is shown. Double pipe and reboilers are shown in their specific format, and again the actual number of shell passes. The following data for each exchanger is shown at the top of the flow diagram:

- The heat exchanger item number. (This is also shown adjacent to the exchanger drawing)
- The title
- The duty of the exchanger (In Btu/hr, or Kcal/hr, etc.)
- Insulation

Air coolers. As in the case of the heat exchangers, air coolers are shown in more detail on the MFD than on the process flow diagram. Usually on the MFD the air cooler is shown as a narrow rectangle. The fan in this case is drawn below the rectangle for a forced draft cooler or above the rectangle in the case of an induced air cooler. Only one process line is shown to and from the cooler but the number of passes is shown on these lines. Any temperature control by louvres or variable pitch fans is shown on the diagram together with the appropriate instrumentation. The following data is given at the top of the MFD above the cooler:

- The cooler item number (this is also shown adjacent to the drawing)
- The title
- Duty of the cooler

Fired heaters. The outline of the furnace is shown as being a cylindrical or a cabin type heater. Most companies carry their own symbols to portray this feature. The actual number of passes is shown on an inlet and outlet header together with the control system for the process flow. Only one pass is shown as entering and leaving the heater however and flowing through the item. The internal flow is shown as a dotted line in the fire box. All instrumentation for the heater is shown in detail—such as temperature points on the heater coil and in the fire box, oxygen analyzers in the chimney and the chimney damper control. Snuffing steam and de-coking manifolds are usually shown as separate details. The firing control system is shown in detail. Usually this follows a standard adopted by the company for all the heaters. All the instrumentation interlocks and safety features are detailed in the MFD for all heaters. The following data is provided for this item at the top of the flow diagram and above each heater:

- The item number
- Title
- Duty of the heater

Pumps. Pumps are shown in much greater detail on the MFD than on the process flow diagram. The pump drawing itself shows the type of pump and the type of driver. For example, a centrifugal pump is shown as a narrow vertical parallel lines curved at both ends and resting on a base plate. A motor driver is shown as a small horizontal rectangle curved at both ends also resting on the base plate and connected to the pump by a short line. Process suction lines enter the center of the pump case and the discharge line leaves from the top of the casing. All pumps are shown in the same detail, that is both normal operating pump and its spare are shown. Process (and utility) lines connecting the pumps in a set are shown together with the valve configuration. Isolating block valves, non-return valves, etc on the pumps are shown together with cooling systems where required. Instrumentation for automatic pump start and stop is also detailed together with electrical switches for manual start/stop facilities. Pumps and other rotary equipment are normally drawn on the bottom of the flow diagram. The data supplied on the MFD for pumps are given below the item on the bottom of the diagram and are as follows:

- Pump item number (followed by “A” for normally operating and “B” for spare pump).
  - ➢ Title
  - ➢ Flow rate (gpm or m^3/hr, etc)
  - ➢ Differential pressure (psi, kPa, etc)

- ➢ SG of pumped fluid at pumping temperature
- ➢ Miscellaneous auxiliary piping (cooling water, flushing oil, seal oil, etc.)

Piping. The MFD is among the most important documents that are developed in the course of a fully engineered project that can proceed to construction and finally to operation. Its importance is probably highest in the case of the piping engineering and design function of a project. For this discipline, the MFD is the basis for all their work. Any piping detail that is required to define the work must appear on this flow diagram if it is to be included at all in the constructed facility. The diagram then becomes a major communication tool for multi discipline interfaces.

In the layout of a MFD, process feed lines should originate at the left hand end of the drawing and the process product lines terminate at the right hand of the drawing. Where this is impractical, origin and terminus of the lines are located for clarity and convenience. The origin and terminus of each process line in any case are identified by a box which shows the descriptive title of the line, the drawing number, and section number of any reference drawing. Where possible process lines between equipment drawings are located either above the line of equipment or below the line of equipment. Every effort in the layout should be made to avoid breaking lines around equipment. Piping high point vents or low point drains are not shown on the MFD unless they have some significant process requirement. Any pertinent requirement for process reasons on any line must be noted. This includes such requirements as no pocketing, sloping, etc. These type of notes are clearly marked on the respective lines.

Utility lines originate and terminate adjacent to the equipment involved. Only the length of line necessary for valves, instrumentation, and line numbering is shown. The utility line origin and terminus are identified by a descriptive title only. (e.g., "LP Steam" and "LP Condensate"). Main utility headers are not shown—these will appear on the "Utility Flow Diagram".

All line sizes are shown on the lines they refer to. Where there is a change in a line size this is also indicated by a "swage" up or down. All valve sizes are indicated on the MFD even if they are line size. Flow direction on all lines (whether process or utility) are clearly shown by directional arrows on the lines. Steam or electrical heat tracing are also indicated on the lines that require it.

Instrumentation. All instrumentation is shown on the MFD in detail. This detail includes:

- Size of control valves
- Instrument hookup method
- Vessel surge levels and level range
- Type of instrument activation (i.e., pneumatic or electronic)

- Computer interface if it applies
- Instrument identification number
- Position of the control valve on air failure (i.e., failed open or closed)

Instrument symbols are usually to ISA standard with some minor modifications to meet the respective company's needs.

The utility flow diagram

Process input to the utility flow diagram development is minor compared with that for the PFD and MFD. It involves the sizing of the utility lines and valves only. The process engineer is responsible to ensure that all the necessary utility lines to satisfy the process have been included. The UFD itself is based on the approved plot layout of the plant and/or plants and is usually prepared by others. It shows the direction of flow and sequence of equipment geographically just as they appear on the plot plan. Although process input to the UFD as such is minor, there will be considerable detail necessary to complete the entire utility picture. For example, the UFD will show an instrument air header serving all the units in the process. This header will originate at the instrument air compressor set and dryers. This origin will only be indicated on the UFD with reference to a detail drawing for the instrument air compressor set. This detail drawing will be a MFD and the process engineer will have the same input and responsibility for this diagram as for any other MFD.

Drawings of sections of all these engineering drawings are given in Appendix A of this volume to illustrate this topic.

Equilibrium flash vaporization (EFV)

When a mixture of compounds vaporizes or condenses, there is an unique relationship between the composition of the mixture in the liquid phase and that in the corresponding phase at any condition of temperature and pressure. This relationship is termed the equilibrium flash vaporization for the mixture. It can be calculated using the composition of the feed mixture and the equilibrium constant of the components in the mixture. This is expressed by the equation:

$$L = \frac{x_{\mathrm{f}}}{1 + (V/L)K}$$

where

L = Total moles/hr of a component in the liquid phase.
x_{f} = Moles/hr of the component in the feed.

V/L = The ratio of total moles vapor to total moles liquid.
K = The equilibrium constant for each component at the flash condition of temperature and pressure.

There are several publications giving values for K. Among these are the charts in Maxwell's "Data Book on Hydrocarbons" which are based on fugacities. Others may be found in engineering data books such as "Gas Processors Suppliers Association" which are based on convergence pressures. A rough and ready substitute for K factors is to use the vapor pressure of the component divided by the system pressure. This, however, should not be used for any definitive design work nor in systems which have azeotropes or are near their critical conditions. A method for calculating equilibrium flash vaporization is given by the following steps.

Step 1. Prepare a table with the first column giving the components making up the feed. The second column will be the composition of the feed in mol/hr. The third column is a listing of the equilibrium constant K for each component at the temperature and pressure of the flash condition. Allow up to three columns following for assumptions of V/L. Each of these three columns should be subdivided into two. The first giving the product of $(V/L)K$ and the second for listing the "L" for each component. Other columns may be added to calculate mole wt of vapor and SG of the liquid phase.
Step 2. Assume a value for V/L. This is a judged assumption but start with 1.0 or 0.1 whichever seems to be the more realistic. Calculate $(V/L)K$ for each component.
Step 3. Calculate "L" for each component from the equation:

$$L = \frac{X_{\mathrm{f}}}{1 + (V/L)K}$$

Step 4. The calculated V/L is now obtained by adding the "L" column and subtracting this value from the total moles of feed in column 1. This subtraction is the vapor moles as calculated. Then the calculated V/L is arrived at by dividing the total V by the total of the "L" column.
Step 5. The calculation is complete when V/L calculated is equal to V/L assumed. An answer within 5% is usually acceptable. If the calculated V's assumed is not within this limit make another assumption for V/L and repeat steps 2, 3, 4. For this second assumption try 5, or 0.5, or 0.05, whichever is more appropriate.
Step 6. If there is still no agreement between assumed and calculated V/L plot the two trial points (assumed Vs calculated) on log graph paper. Draw a straight line through these two points and note where on this line assumed V/L = calculated V/L. This value is the next assumed V/L. Repeat the calculation Steps 2–4 using this value; this usually completes the calculation. If it does not then check that the conditions for the flash are within the boiling point and condensing point for the feed.

In this example, it is required to determine the amount of vapor and liquid and their composition in a feed to a fractionator at 112 psig and 300°F.

			1st Trial $V/L = 0.5$		2nd Trial V/L = 0.2		3rd Trial V/L = 0.1					
	Moles/ hr °F	127 psia K 300°F	V/LK	$L = 1 + \frac{F}{V/LK}$	V/LK	$L = 1 + \frac{F}{V/LK}$	V/LK	$L = 1 + \frac{F}{V/LK}$	MW	Liquid lbs/hr	lbs/gal	GPH
C_2	6.4	9.1	4.55	1.15	1.82	2.27	0.9	3.37	30	101	2.97	34
C_3	43.5	5.0	2.50	12.43	1.00	21.75	0.5	29.0	44	1,276	4.69	301.7
iC_4	16.9	3.3	1.65	44.79	0.66	10.18	0.33	12.71	58	737	4.69	157.1
nC_4	67.6	2.9	1.45	30.04	0.58	42.78	0.29	52.40	58	3,039	4.87	624.0
iC_5	80.5	1.8	0.90	42.37	0.26	59.19	0.18	68.22	72	4,912	5.21	942.8
nC_5	34.6	1.6	0.80	19.22	0.32	26.21	0.16	29.83	72	2,148	5.26	408.4
C_6	124.9	0.85	0.425	87.65	0.17	106.75	0.085	115.12	86	9,900	5.54	1,787.0
C_7	140.9	0.48	0.240	113.63	0.096	128.56	0.048	134.45	100	13,445	5.74	2,342.3
NP260	99.8	0.212	0.106	90.24	0.042	95.74	0.021	97.75	114	11,144	6.18	1,803.2
NP300	99.8	0.116	0.058	94.33	0.023	97.54	0.012	98.62	126	12,426	6.37	1,950.7
NP340	60.4	0.063	0.032	58.53	0.126	59.55	0.006	60.04	136	8,165	6.46	1,263.9
NP382	29.8	0.035	0.0175	29.29	0.007	29.60	0.004	29.80	152	4,530	6.56	690.5
Total	805.1			623.67		680.07		731.31	98.2	71,823	5.4	12,305.6
Calculated V/L				0.29		0.184		0.1				°API = 70

lbs/hr liquid = 71,823 lbs/gal = 5.4
lbs/hr vapor = 4,998 mol wt = 67.7
lbs/hr feed = 76821

Note the components NP260 to NP382 are psuedo components having mid boiling points of 260, 300, 340, and 382°F, respectively. K for these components are based on their vapor pressure and system pressure relationship.

Predicting the EFV curve from TBP data. For crude oils and complex mixtures such as the heavy products the equilibrium vaporization curve can be calculated from the TBP curve using empirical methods given by Edmister or Maxwell. In this work the EFV is based on the method by Maxwell in his book "*Hydrocarbon Data*". This method has been described in Chapter 1 of this Handbook.

F

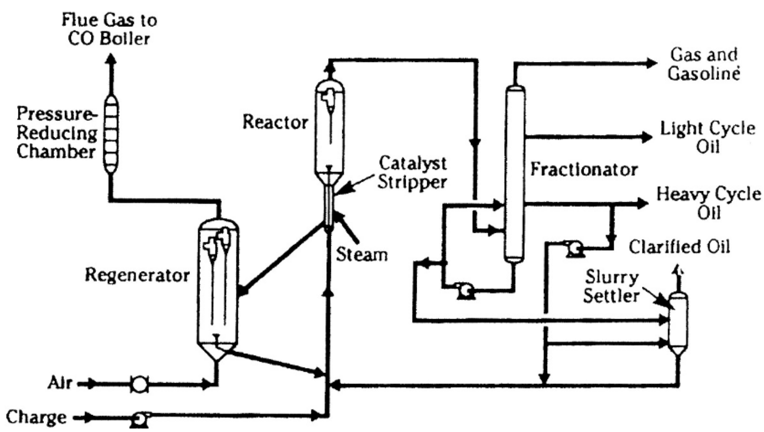
FCCU (The fluid catalytic cracking unit)

Introduction and a brief history of the process. The Fluid Catalyst Cracking Unit (FCCU) is a process for converting middle and heavy distillates to high-octane

gasoline and olefin-rich light gases. It was developed during World War II to provide the high-octane fuel required by the war effort. The first unit of its kind was brought on stream in the USA in 1942. These first models of the process were a side-by-side reactor/regenerator configuration. The transfer line for the catalyst between the two items was relatively short and the design as such was aimed at concentrating the reaction in the reactor's fluid bed. To achieve effective transfer of the catalyst between the two items the reactor was operated at a slightly higher pressure than the regenerator and the regenerator elevated to provide the hydraulic head. A series of slide valves provided the control of catalyst flow between the two units.

The catalysts used in these early units were simply finely ground silica alumina. These had poor fluidization characteristics and were fragile producing a high quantity of fines. The conversion rate with this type of catalyst was also low at about + or −50LV%. After the war and during the 1950's the development of catalytic reforming of straight run naphtha with its additional bonus of cheap hydrogen reduced the popularity of the FCCU considerably. Its revival as the accepted 'work horse' of refining came with the development of riser cracking and the use of zeolite catalysts during the early 1960s. These two developments projected the process back to its prominence principally because it could upgrade low quality products to high quality gasoline and LPG cheaply and at high conversion. Today it still remains a principal process in heavy oil processing. Further advances in catalyst management and in the process itself provides a unit which can convert certain atmospheric and vacuum residues directly to more valuable products. A complete description of the process with details of its chemistry and reactor mechanism is given in Chapter 6 of this Handbook. The following is a summary of the process reactor side mechanism.

Process description



"A typical 'side by side' fluid catalytic cracking unit".

The “heart” of the process consists of reactor vessel and a regenerator vessel interconnected to allow the transfer of spent catalyst from the reactor to the regenerator and of regenerated catalysts back to the reactor. The heat for the oil cracking is supplied by exothermic heat of the catalyst regeneration. This heat is transferred by the regenerated fluid catalyst stream itself. The oil streams (feed and recycle) are introduced into this hot catalyst stream on route to the reactor. Much of the cracking occurs in the dispersed catalysed phase along this transfer line or riser.

The final contact with catalyst bed in the reactor completes the cracking mechanism. The vaporized cracked oil from the reactor is suitably separated from entrained catalyst particles (by cyclone) and routed to the recovery section of the unit. Here it is fractionated by conventional means to meet the product stream requirements. The spent catalyst is routed from the reactor to the regenerator after separation from entrained oil. Air is introduced into the regenerator and the fluid bed of the catalyst. The air reacts with the carbon coating on the catalyst to form CO/CO_2. The hot and essentially carbon free catalyst completes the cycle by its return to the reactor. The flue gas leaving the regenerator is rich in CO. This stream is often routed to a specially designed steam generator where the CO is converted to CO_2 and the exothermic heat of reaction used for generating steam (the CO boiler). Alternatively, CO combustion promoters may be used within the regenerator.

Feed stocks to the FCCU are primarily in the heavy vacuum gas oil range. Typical boiling ranges are 640°F (10%) to 980°F (90%). This gas oil is limited in end point by maximum tolerable metals, although the new zeolite catalysts have demonstrated higher metals tolerance than the older silica–alumina catalysts. The process has considerable flexibility. Apart from processing the more conventional waxy distillates to produce gasoline and other fuel components, feed stocks ranging from naphtha to suitably pretreated residuum are successfully processed to meet specific product requirement.

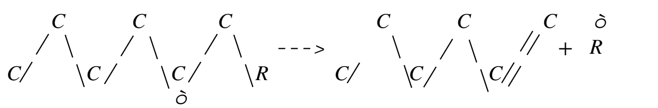
A summary of the mechanism of fluid catalytic cracking. The feed stock to FCCUs are usually the higher distillates of the crude barrel. The feed stock in this range of material therefore contains compounds of complex structure, some of which are contaminated by inorganic molecules such as sulfur, metals (vanadium, sodium, nickel, and the like). The amounts of these contaminants will vary for different crudes and the boiling range of the feed. The feed stock will also demonstrate a differing ease to its ability to crack under the conditions of the FCCU.

The mechanism of the cracking itself is extremely complex, and many theories have been offered to account for this. Certainly under the high temperature conditions of the FCC reactor, one can expect thermal cracking to occur, and to some extent this happens. Thermal cracking however results in the random fracture of the hydrocarbon compounds and there is very little selectivity in the resulting product content and yields. This is not the case in Fluid Catalytic cracking, indeed one of the process’s

main attraction is its high selectivity in its product make. The most generally accepted theory for this is the carbonium ion mechanism. It is believed that the carbonium ion in this cracking mechanism is initiated from an olefin's early contact with the catalyst at the high riser temperature condition. Once formed the ion reacts to:

- Crack larger molecules to smaller ones
- React with other molecules
- Isomerize
- React with the catalyst to terminate a chain

The cracking reaction then tends to follow the following route where the C—C bond in the β position relative to the carbonium ion is severed to form the olefin and the reactive positively charged ion. This is illustrated as follows:



Carbonium ion *Olefin* *Carbonium ion*

The olefin may form new carbonium ions while the R ion reacts to form secondary and tertiary carbonium ions. The tertiary ion is the more stable, and is probably the more active in this cracking mechanism. A more detailed account of this mechanism is provided by Venuto P.B. and Habib E.T. in their paper "Catalyst–feed stock—engineering interactions in Fluid Catalytic Cracking".

Formation of coke on the catalyst. The formation of coke on the catalyst is an unavoidable occurrence of the catalytic cracking process. The mechanism of the coke formation is also very complex as was the case in the cracking mechanism itself. It is likely that coke is formed by the dehydrogenation and condensation of poly aromatics and olefins. Its deposition on the catalyst however tends to block the active pores which will reduce the effectiveness of the catalyst. The only recourse to this is to burn off the coke with air to form CO and CO_2. The heat of reaction for this coke burn off becomes important to the process as it provides the heat of reaction on its transfer from the regenerator to the reactor riser.

Typical yields and the effect of feedstock types. This item gives typical yield structures for various FCCU feed stocks and severities of operation. These were based on 100% zeolite catalyst processes and are included here as a guide to conventional FCCU process capability.

Note while these data may be used in study work and comparative process analysis, they should not be used for any definitive design work. For this definitive work specific licensor data from pilot plant test runs on the design feed stock must be used.

Hydrotreated Gas Oil (520–630°F)

Conversion vol%	50	60	70
Yields vol%:			
Gas	3.8	4.0	4.2
Propylene	4.3	6.0	8.0
Butylene	6.9	10.0	17.5
Propane	2.5	2.7	3.0
i-Butane	3.6	5.0	7.5
n-Butane	1.5	1.6	1.8
C_5-Naphtha	28.9	31.4	34.6
Light cycle oil	44.5	35.9	26.0
Heavy cycle oil	2.2	2.2	2.2
H_2S wt%	1.2	1.2	1.2

Straight Run Diesel (520–650)

Conversion vol%	30	40	50
Yields vol%:			
Gas	3.0	3.3	3.9
Propylene	3.0	4.2	6.0
Butylene	5.5	6.1	8.4
Propane	2.0	2.4	2.8
i-Butane	2.4	3.8	5.2
n-Butane	1.3	1.4	1.6
C_5-Naphtha	17.5	20.0	23.0
Light cycle oil	68.5	54.5	49.0
Heavy cycle oil	2.8	2.8	2.8
H_2S wt%	1.4	1.4	1.4

Hydrocracker Gas Oil (650–750°)

Conversion vol%	70	80	90
Yields vol% :			
Gas	4.2	4.8	5.0
Propylene	8.0	10.0	13.0
Butylene	15.0	24.0	41.0
Propane	3.1	3.5	3.9
i-Butane	7.0	9.0	12.0
n-Butane	1.5	1.8	2.3
C_5-Naphtha	40.0	49.5	52.0
Light cycle oil	23.0	16.0	9.0
Heavy cycle oil	3.0	3.0	3.0
H_2S wt%	1.1	1.1	1.1

Hydrotreated Visbreaker Gas Oil (380–650°F)

Conversion vol%	60	70	80
Yields vol% :			
Gas	3.0	3.6	4.0
Propylene	3.8	5.0	6.8
Butylene	5.0	6.8	8.0
Propane	2.0	2.3	3.0
i-Butane	2.6	4.0	6.0
n-Butane	1.6	1.8	1.9
C_5-Naphtha	50.0	53.0	60.0
Light cycle oil	37.0	28.5	18.5
Heavy cycle oil	2.0	2.0	2.0
H_2S wt%	←———	Neg	———→

Fired heaters

Generally fired heaters fall into two major categories:

- Horizontal type
- Vertical type

The horizontal type heater usually means a box type heater with the tubes running horizontally along the walls. Vertical type is normally a cylindrical heater containing vertical tubes. Full details of both these heater types are given in Chapter 18.

Horizontal box types are preferred for crude oil heaters, although vertical cylindrical have been used in this service. Vacuum unit heaters should have horizontal tubes to eliminate the static head pressure at the bottom of vertical tubes and to reduce the possibility of two-phase slugging in the large exit tubes. Occasionally, several different services ("coils") may be placed in a single heater with a cost saving. This is possible if the services are closely tied to each other in the process. Catalytic reforming pre-heater and re-heaters in one casing is an example. Reactor heater and stripper reboiler in one casing is another example. This arrangement is made possible by using a refractory partition wall to separate the radiant coils. The separate radiant coils may be controlled separately over a wide range of conditions by means of their own controls and burners. If a convection section is used, it is usually common to the several services. If maintenance on one coil is required, the entire heater must be shut down. Also, the range of controllability is less than with separate heaters.

Each of these types may be shop fabricated if size permits. Shop fabrication reduces costs. However, shop fabrication should not be forced to the extent of getting an improperly proportioned heater.

As fired heaters have a live source of energy they are designed and manufactured to strict codes. Details of these are also given in Chapter 18. These codes set the parameters for heater tube thickness, tube, and heater dimension, Inspection requirements, and fire protection.

Thermal rating. Thermal rating of fired heaters is a complicated and specialized procedure. While this procedure is described in Chapter 18 it is not detailed. For most basic design and evaluation studies the following rules of thumb may be used:

	Btu/hr sqft
Horizontal, fired on one side	8,000–12,000
Vertical, fired on one side from bottom	9,000–12,000
Vertical, single row, fired on both sides	13,000–18,000

Heater efficiency. The efficiency of a fired heater is the ratio of the heat absorbed by the process fluid to the heat released by combustion of the fuel expressed as a percentage.

Heat release may be based on the LHV (Lower Heating Value) of the fuel or HHV (Higher Heating Value). Process heaters are usually based on LHV and boilers on HHV. The HHV efficiency is lower than the LHV efficiency by the ratio of the two heating values.

Heat is wasted from a fired heater in two ways:

- with the hot stack gas
- by radiation and convection from the setting

The major loss is by the heat contained in the stack gas. The temperature of the stack gas is determined by the temperature of the incoming process fluid unless an air preheater is used. The closest economical approach to process fluid is about 100°F. If the major process stream is very hot at the inlet, it may be possible to find a colder process stream to pass through the convection section to improve efficiency, provided plant control, and flexibility are adequately provided for. A more common method of improving efficiency is to generate and/or superheat steam and preheat boiler feed water. The lowest stack temperature that can be used is determined by the dew point of the stack gases. The figures in Chapter 18 may be used to estimate flue gas heat loss. Heat loss from the setting, called radiation loss, is about $1\frac{1}{2}$ to 2% of the heat release.

The range of efficiencies is approximately as follows:

Very high −90%+. Large boilers and process heaters with air pre-heaters.
High −85%. Large heaters with low process inlet temperatures and/or air pre-heaters.

Usual—70–80%.
Low—60%.

Burners. The purpose of a burner is to mix fuel and air to ensure complete combustion. There are about 12 basic burner designs. These are:

Direction —	vertical up fired
	vertical down fired
	horizontally fired
Capacity —	high
	low
Fuel type —	gas
	oil
	combination
Flame shape —	normal
	slant
	thin, fan-shaped
	flat
	adaptable pattern
Hydrogen content —	high
Excess air —	normal
	low
Atomization —	steam
	mechanical
	air assisted mechanical
Boiler types	
Low NO_x	
High intensity	

Various combinations of the above types are available.

Details of gas, oil, and combination burners are given in Chapter 18, together with burner controls and heater noise.

Chapter 18 under the section on fired heaters continues with a description and discussion on refractories, stacks, and stack emission. Finally the chapter describes the specification for a typical fired heater.

Flash points

The flash point is a measure of the tendency of the, material to form a flammable mixture with air under controlled laboratory conditions. It is however only one of several properties that must be considered in assessing the overall flammable hazard of

the material. The flash point is used to establish the flammable criteria in transporting the material. Generally shipping and safety regulations will be based on the flash point criteria. The flash point should not however be used to describe or appraise the fire hazard or risk under actual fire conditions. Test method (D93 provides the closed cup flash point test procedures for temperatures up to 698°F). Details of the apparatus used and the laboratory method for determining a flash point is given in Chapter 16 of this Handbook. The flash point of two or more blended components is determined by the volume composition of the components in the blend and the use of the flash point index curve. This method and the index curve is given in Chapter 1 of this Handbook. A simple estimate of a material's flash point can be calculated from its ASTM distillation by the equation:

$$\text{Flash Point}\,^\circ\text{F} = 0.77(\text{ASTM } 5\% - 150^\circ\text{F}).$$

Flash zone

A flash zone is associated with the distillation of crude oil, both atmospheric and vacuum, the main fractionating towers of the fluid catalytic cracking unit, visbreaker or thermal cracking units. The flash zone is the area in these distillation towers where the distillate vapors are allowed to separate from the un-vaporized liquid. The transfer line from the heater enters the flash zone. The vapors rise up through the tower to be condensed by cold reflux streams coming down. Steam enters the flash zone from the bottom product stripper section located below the flash zone.

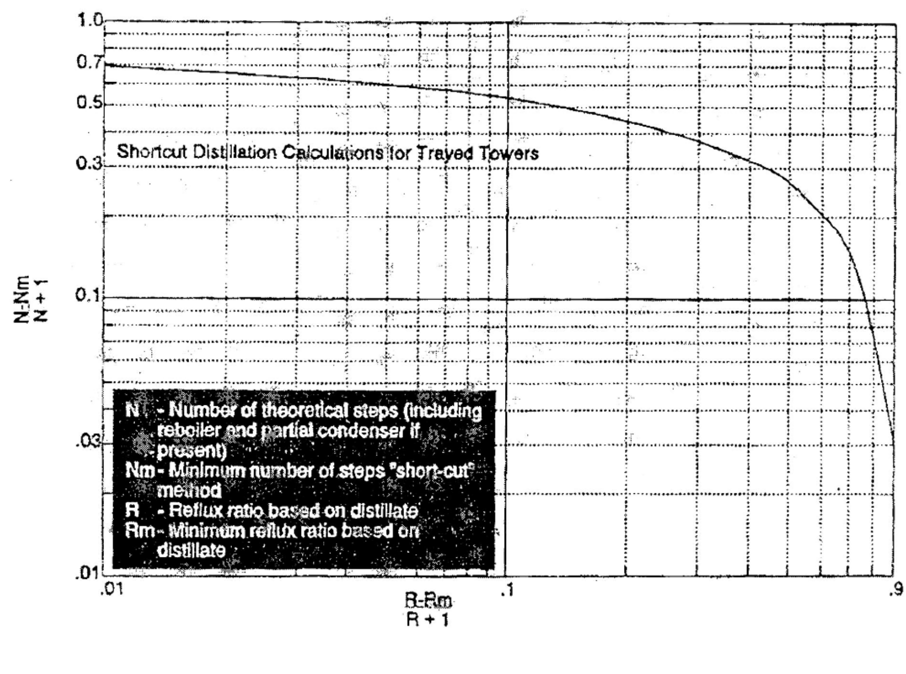
Flash zone conditions, particularly flash zone temperature is difficult to measure accurately. This is due to the profiles set up in the flash zone by turbulence of the feed entering and vapor disengaging. Knowledge of flash zone conditions is, however, essential when designing these units, evaluating their performance or trouble shooting them. The item in Chapter 3 of this Handbook deals with a calculation procedure to establish these flash zone conditions for atmospheric and vacuum distillation crude distillation towers.

Fractionation

This is a unit operation in chemical engineering which separates components from mixtures in which they are contained. In petroleum refining this separation process is a major means of separating precise groups of petroleum components from the crude oil feed and other intermediate refining processes. Separation by fractionation is accomplished by heat and mass transfer on successive stages represented by carefully designed trays. These trays are designed to enhance the heat and mass transfer by good mixing of hot vapors rising through the trays with colder liquid entering the tray. The mixing tends to achieve a phase equilibrium between the liquid and vapor traffic.

Fractionation as a separating tool is used extensively throughout the process industry. It can be a simple process separating just two components (such as water and alcohol) of very complex separation of multi components. It is the later that is required in the petroleum processing industry. The calculation of the number of stages required for the simple binary fractionation can be accomplished graphically using the McCabe Thiele diagram, the number of stages required for the multi-component separation is achieved by using a number of complex equations, and the individual equilibrium constants for the various components. The rigorous method for calculating the number of fractionation stages in multi component separation is by stage to stage calculation with 'trial and error' determination of the temperature and pressure conditions on each stage. The calculation is complete when convergence of phase equilibria is met on the feed input stage. This is the method used in developing the computer simulation program for multi-component fractionation.

The method is simplified for manual computation by a correlation developed by Gilliland (reference Maxwell's Data Book on Hydrocarbons). This is a correlation which relates minimum stages at total reflux to minimum reflux at infinite number of stages. Figure 4.2, Chapter 4, is reproduced below to show this correlation.



The Gilliland correlation for calculating theoretical trays.

Where:

N = actual number of trays.
N_m = minimum number of stages at total reflux.
R = actual reflux
R_m = minimum reflux at infinite number of stages.

There are two equations that define the items R_m and N_m these are:

- The *Fenske equation* which is used to calculate the minimum trays at total reflux.

$$\mathrm{N}_{\mathrm{m}+1} = \mathrm{Log}\left[\left(\frac{\text{Lt Key}}{\text{Hy Key}}\right)_{\mathrm{D}} \cdot \left(\frac{\text{Hy Key}}{\text{Lt Key}}\right)_{\mathrm{W}}\right] \div \mathrm{Log}\,\phi$$

Where:

N_{M} = minimum number of theoretical strays at total reflux. The + 1 is the reboiler which is counted as a theoretical tray
LT Key = is the mole fraction of the selected light key
HY Key = is the mole fraction of the selected heavy key
D = fractions in the distillate product
W = fractions in the bottom product
ϕ = KLt Key/Khy key
KLt key = the equilibrium constant of the light key at mean system condition of temperature and pressure
KHy key = the equilibrium constant of the heavy key again at mean system conditions

- *The Underwood equation* which establishes the minimum reflux at infinite stages. The Underwood equation is more complex than the Fenske equation and requires trial and error method for its solution. The equation itself is in two parts. The first looks at the vapor volatility (ratio of K's) of each component in the feed to one of the selected keys. Then by trial and error arriving at an expression for a factor 'B' that forces the equation to zero.
  This first equation is written as follows:

$$\frac{\Sigma(\phi \mathrm{i})(X_{\mathrm{i}}F)}{X_{\mathrm{i}}F - B} = 0$$

ϕ_i = is the relative volatility of component i
X_iF = is the mole fraction of component i in the feed
B = is the factor that forces the sum of the expression for each component to zero

The second equation uses the Factor B calculated from the first equation to determine the minimum reflux. This equation is

$$R_{\mathrm{m}+1} = \frac{\Sigma(\phi_i)(X_i D)}{X_i D - B}$$

where

ϕi = is the relative volatility of component i
$X_i D$ = is the mole fraction of component i in the distillate
B = is the factor obtained from first equation
R_{m} = minimum reflux at infinite trays ($R_{\mathrm{m}+1}$ include the reboiler)

R is taken as $1.5 \times R_{\mathrm{m}}$ while N is taken as $1.5 \times N_{\mathrm{m}}$.

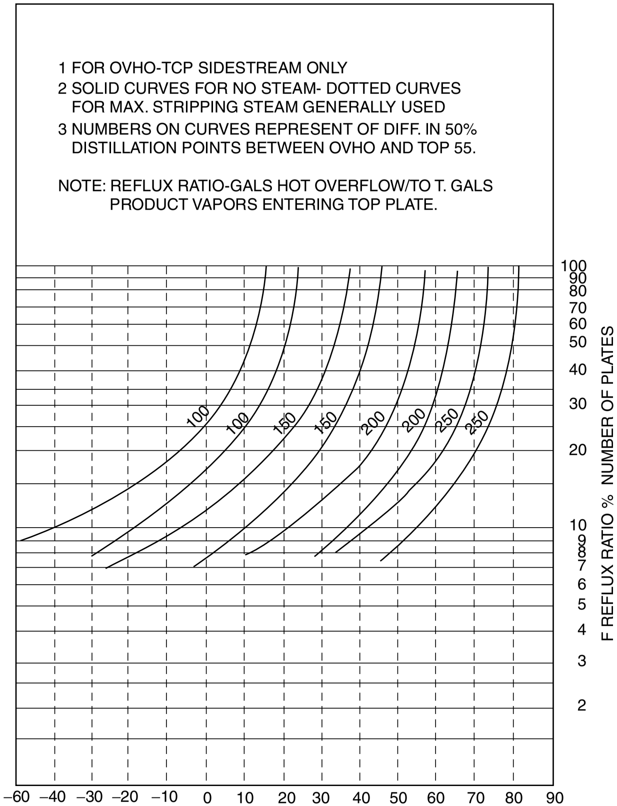
Fractionation in the atmospheric and vacuum crude distillation towers

The method of Gilliland is impractical for use in the complex fractionation that is experienced in the main refinery towers handling the crude feed and other similar streams in the refining process. Packie J.W. developed an empirical method based on ASTM distillation gaps to define the fractionation between adjacent cuts. This degree of fractionation is measured by the temperature difference between the ASTM 95% of the lighter cut and the 5% temperature of the adjacent heavier cut. These differences can be positive or negative. That is the 5% temperature of the heavier cut can be higher than the 95% temperature of the lighter cut. This difference is called an *ASTM Gap.* On the other hand some adjacent cuts may demonstrate the reverse that is the 5% temperature of the heavier cut may be lower than the 95% temperature of the lighter cut. This difference is called an *ASTM Overlap.* Thus in a typical crude unit specification the fractionation may be quoted as follows:

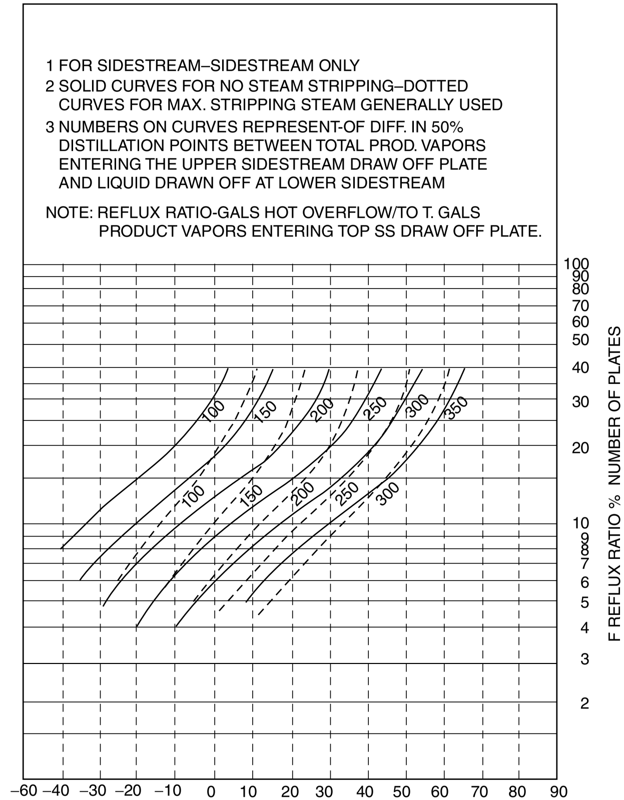
The fractionation in the crude atmospheric distillation tower shall be:

95% naphtha ASTM temperature and the 5% temperature of the kero shall have a gap of 25°F.
95% kero ASTM temperature and the light gas oil 5% temperature shall have a gap of 0°F.
95% LGO ASTM temperature and the heavy gas oil 5%temperature shall have an overlap of no more than 15°F (a –15°F gap).

The number of the fractionation trays required to meet the respective fractionation gaps (overlaps) between cut draw-off in these main columns is based on a correlation. This correlation is a series of curves based on the 50% distillation temperature difference between the total vapor entering the draw off tray and the liquid leaving the tray. There are two sets of these curves, the first with steam present and the second based on no



Fractionation Curves for Overhead to Top Sidestream Products.



Fractionation Curves for Sidestream to Sidestream Products.

ASTM gaps and overlaps.

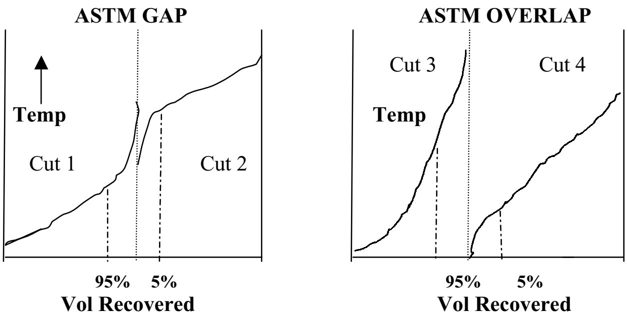
steam. On the basis of these curves the reflux rate times the number of stages are read off for the required ASTM gaps.

A copy of this correlation is given in Chapter 3 Appendix 1. For convenience it is also printed on page 1169.

G

Gaps and overlaps

Gaps and overlaps refer to the difference between the temperatures of the 95 vol% recovered in a lighter cut and the 5 vol% recovered of the adjacent heavier cut based on their ASTM distillation. The following diagrams illustrate this concept:



The ASTM Gap shown above would be typical in the separation between naphtha and kero in the atmospheric distillation unit. The 5% temperature of the kero (cut 2) is higher than the naphtha (cut 1) 95% temperature. This is a good separation because there are few kero components in the heavy end of the naphtha. The overlap illustration is typical of the separation between the heavier products of the atmospheric distillation of crude oil such as between light gas oil cut and the heavy gas oil cut. A GAP then is when the numeric difference between the 5% of the heavier cut and the 95% of the lighter cut is positive. An OVERLAP is when this difference is negative.

The ASTM gap and overlaps are used as a measure of fractionation. Packie (*Am Inst Chem Eng Transactions Vol 317*) *1941* has related a series of Gaps and overlaps to the 50% temperature difference between the vapors rising through a distillation tray and the liquid leaving. These series of curves are related to gaps and overlaps to give a product of reflux times number of trays. The series of curves have also been constructed for a 'No steam system' and 'Maximum steam system'. Two of these curves are shown under section "F" preceding.

Gas-refinery fuel

The gas fractions in petroleum refining may be taken as that fraction on crude or produced in a process as boiling below propane. This vapor fraction is usually used as a fuel to the refinery's fired heaters. The heaters themselves have burners on dual heating source, either fuel oil or fuel gas. The pilot flames on all the heater burner assemblies are on fuel gas.

The fuel gas is the collection of the vapors from the appropriate overhead distillation condensers, purge gas streams (from the hydro-treating processes), and any other continuous hydrocarbon gas stream meeting the fuel gas criteria. Emergency venting and start up purge streams are routed to the refinery flare system. The fuel gas streams are stored in bullets with heating coils to vaporize the heavier components in the mixture (i.e., butanes and occasionally pentanes). With the introduction of the 'clean air act' the fuel gas stream must be treated for the removal of sulfur. This is accomplished by absorption of the sulfur components (hydrogen sulfide, and possibly mercaptans) into amine solutions or other absorbents. See the item on gas treating in Chapters 10 and 15.

Gas oil

Usually there will be two gas oil side streams, a light gas oil side stream and, below this take off, a heavy gas oil side stream. Both these side streams are steam stripped to meet their respective flash point specification (usually 150°F minimum). The lighter side stream cut of about 480–610°F on crude) is the principal precursor for the automotive diesel grade finished product, this side stream is desulfurized to meet the diesel sulfur specification in a hydrotreater (see Chapter 8). The lower gas oil stream is really a guard stream to correct the diesel distillation end point. This heavy gas oil may also be hydrodesulfurized and routed to either the fuel oil pool (as a precursor for marine diesel for example) or to a finished heating oil product from the gas oil pool. See also Chapter 2.

Gasolines

These are probably among the most important and controversial refinery products. This is due to the fact that they are readily and widely used by the general public and are growing more and more in demand as the automobile industry expands. With this expansion in demand and their use as fuels, augmented are those problems associated with their effect on the environment and the health hazards due to emission from vehicles. These have become major concerns in most highly developed countries of the world.

Two major gasoline products are produced in the petroleum refinery. Their specification and standard quality are fully described and discussed in Chapters 2, 9, and 15. The two grades shipped from refineries are usually a regular grade with an octane number of 87 and a premium grade with an octane number of 93. These octane levels may differ slightly from country to country, but these are the key quality for North America, with octane numbers defined as (RON + MON)/2.

Gasolines are processed from the catalytic reforming of a heavy straight run naphtha 190–360°F cut. This cut is the bottom product of a naphtha splitter which takes as fee the de-butanized overhead distillate from the crude unit. The top distillate product from this splitter will be a light straight run naphtha. This will be blended with other components (such as the reformate, catalytic cracked naphtha, and other octane) enhancement cuts to make the specified two gasoline refinery products.

The catalytic reformer is run to make a 91–100 octane number research reformate after the removal of butanes and lighter. Prior to the clean air of the 1960s, tetra ethyl lead was used extensively as an octane enhancer, and the reformer operating severity in terms of octane number was much reduced. The clean air act prohibits the use of the lead compound and now only lead free gasoline is used in all vehicles. More stringent controls are becoming to the fore in environmental controls in most of the developed countries. Among these are the further reduction of sulfur compounds in gasoline and perhaps even more important the reduction of aromatic compounds in the products. The development of higher blending stock such as the oxygenated gasoline and the increased production and use of paraffin isomers make this a very possible achievement. These are detailed in Chapter 9 and Chapter 15.

Gas treating processes

Refinery gas treating usually refers to the process used to remove the so called ‘Acid Gasses’ which are hydrogen sulfide and carbon dioxide from the refinery gas streams. These acid gas removal processes used in the refinery are required either to purify a gas stream for further use in a process or for environmental reasons associated with the use of the gas for fuel. Clean air legislation now being practiced through most industrial countries requires the removal of these acid gases to very low concentrations in all gaseous effluent to the atmosphere. Hydrogen sulfide combines with the atmosphere to form very dilute sulfuric acid and carbon dioxide forms carbonic acid both of which are considered injurious to personal health. These compounds also cause excessive corrosion to metals and metallic objects and may contribute to “global warming.”

The use of chemically “basic” liquids to react with the acidic gases was developed in 1930. The chemical used initially was tri-ethanolamine (TEA). However in more recent times as mono-ethanolamine (MEA) has become commercially the more

available and preferred liquid reactant due to its high acid gas absorbency on a unit basis. Numerous alternative processes to MEA have been developed. These have fewer corrosion problems and are to a large extent more energy efficient. Inhibitor systems have however been developed which have eliminated much of the MEA corrosion problems. Some of these newer processes also are designed to remove the H_2S leaving the CO_2 to remain in the gas stream.

In an amine treating unit sour gas (rich in H_2S) enters the bottom of the trayed absorber (or contactor). Lean amine is introduced at the top tray of the absorber section to move down the column. Contact between the gas and amine liquid on the trays results in the H_2S in the gas being absorbed into the amine. The sweet gas is water washed to remove any entrained amine before leaving the top of the contactor.

Rich amine leaves the bottom of the contactor to enter a surge drum. If the contactor pressure is high enough a flash stream of H_2S can be routed from the drum to a trayed stripper. The liquid from the drum is preheated before entering a stripping column on the top stripping tray. This stripper is reboiled with 50 psig saturated steam. Saturated 50 psig steam is used because higher temperatures cause amines to break down. The H_2S is stripped off and leaves the reflux drum usually to a sulfur production plant. Sulfur is produced in this plant by burning H_2S with a controlled air stream. The lean amine leaves the stripper bottom and is cooled. The cooled stream is routed to the contactor.

There are several liquid solvents in commercial use for the removal of H_2S and CO_2 from refinery gases. Among the more common are the amines. These include:

MEA — Mono-ethanolamine
DEA — Di-ethanolamine
DGA — Di-glycolamine

In addition to these amine base solvents there are also the hot potassium carbonate process (Benfield), Sulfinol and ADIP. These latter two processes are marketed by the Shell company and are quite common in world wide usage. Full details of the more common of these compounds together with the reaction mechanism are given in Chapter 10. A comparison of these compounds and their properties are given in Table 19.G.1.

Grids

Grids are used as low pressure drop packing in certain fractionation towers. They came into prominence with the development of the crude oil ‘dry vacuum’ units. See Chapter 3 and Chapter 18 for details of this type of packing and its use.

Table 19.G.1. A comparison of gas treating absorbents

	*MEA	*DEA	*DGA	*DIPA	Sulfinol	*Sulfolane
Molecular wt	61.1	105.1	105.14	133.19		120.17
Boiling point, °F	338.5	515.1	405.5	479.7		545
Boiling range, 5–95%,	336.7–341.06	232–336.7	205–230	–		–
Freezing point, °F	50.5	77.2	9.5	107.6		81.7
Sp. gr., 77°F	1.0113	1.0881	1.0572	–		1.256
140°F	0.9844	(86°F) 1.0693	1.022	0.981 (129°F)		(86°F) 1.235
Pounds per gallon, 77°F	8.45	9.09 (86°F)	8.82	8.3 (86°F)		10.46 (86°F)
Abs. visc., cps., 77°F	18.95	351.9	40	870 (86°F)		12.1 (86°F)
140°F	5.03	(86°F) 53.85	6.8	86 (129°F)		4.9
Flash point, °F	200	295	260	255		350
Fire point, °F	205	330	285	275		380
Sp. ht. Btu/lb, °F	0.663	0.605	0.571	0.815		0.35
Critical–temp., °F	646.3	827.8	765.6	–		982.4
Critical–press., atm.	44.1	32.3	37.22	–		52.2
Ht. of vaporize., Btu/lb	357.94	267.00	219.14	202.72		225.7
Ht. of reaction–CO_2 Btu/lb (Approx)	825	620	850		580	
Ht. of reaction–H_2S, Btu/lb (Approx)	650	550	674		500	

*MEA = $HOC_2H_4NH_2$
*DEA = $(HOC_2H_4)_2NH$
*DGA = $HOCH_2OCH_2C_2H_4NH_2$
*DIPA = $(HOC_3H_6)_2NH$
*SULFOLANE = $(CH_2)_4SO_2$

H

Heaters

Heaters are used extensively in petroleum refining to provide heat energy to the process plants utilizing an independent energy source namely fuel oil or fuel gas. Generally fired heaters fall into two major categories:

- Horizontal type
- Vertical type

The horizontal type heater usually means a box type heater with the tubes running horizontally along the walls. Vertical type is normally a cylindrical heater

containing vertical tubes. Figures 18.47 and 18.48 show examples of these two types of heaters.

Cylindrical heaters require less plot space and are usually less expensive. They also have better radiant symmetry than the horizontal type.

Horizontal box types are preferred for crude oil heaters, although vertical cylindrical have been used in this service. Vacuum unit heaters should have horizontal tubes to eliminate the static head pressure at the bottom of vertical tubes and to reduce the possibility of two-phase slugging in the large exit tubes.

Occasionally, several different services ("coils") may be placed in a single heater with a cost saving. This is possible if the services are closely tied to each other in the process. Catalytic reforming preheater and reheaters in one casing is an example. Reactor heater and stripper reboiler in one casing is another example. This arrangement is made possible by using a refractory partition wall to separate the radiant coils. The separate radiant coils may be controlled separately over a wide range of conditions by means of their own controls and burners. If a convection section is used, it is usually common to the several services. If maintenance on one coil is required, the entire heater must be shut down. Also, the range of controllability is less than with separate heaters.

Full details of the two types of heaters are given in Chapter 18 of this book. This includes the mandatory codes that apply to all fired heaters for their fabrication and operation.

Heater burners

Gas burners. The two most common types of gas burners are the "pre-mix" and the "raw gas" burners. Premix burners are preferred because they have better "linearity", i.e., excess air remains almost constant at turndown. With this type, most of the air is drawn in through an adjustable "air register" and mixes with the fuel in the furnace firebox. This is called secondary air. A small part of the air is drawn in through the "primary air register" and mixed with the fuel in a tube before it flows into the furnace firebox. A turndown of 10:1 can be achieved with 25 psig hydrocarbon fuels. A more normal turndown is 3 : 1.

Oil burners. An oil burner "gun" consists of an inner tube through which the oil flows and an outer tube for the atomizing agent, usually steam. The oil sprays through an orifice into a mixing chamber. Steam also flows through orifices into the mixing chamber. An oil-steam emulsion is formed in the mixing chamber and then flows

through orifices in the burner tip and then out into the furnace firebox. The tip, mixing chamber, and inner and outer tubes can be disassembled for cleaning.

Oil pressure is normally about 140–150 psig at the burner, but can be lower or higher. Lower pressure requires larger burner tips, the pressure of the available atomizing steam may determine the oil pressure.

Atomizing steam should be at least 100 psig at the burner valve and at least 20–30 psi above the oil pressure. Atomizing steam consumption will be about 0.15–0.25 lbs steam/lb oil, but the steam lines should be sized for 0.5.

Combination burners. This type of burner will burn either gas or oil. It is better if they are not operated to burn both fuels at the same time because the chemistry of gas combustion is different from that of oil combustion. Gases burn by progressive oxidation and oils by cracking. If gas and oil are burned simultaneously in the same burner, the flame volume will be twice that of either fuel alone.

Pilots. Pilots are usually required on oil fired heaters. Pilots are fired with fuel gas and are not required when heaters are gas fired only, but minimum flow bypasses around the fuel gas control valves are used to prevent the automatic controls from extinguishing burner flames.

More details on fired heater burners are given in Chapter 18 of this Handbook.

Heater efficiencies

The efficiency of a fired heater is the ratio of the heat absorbed by the process fluid to the heat released by combustion of the fuel expressed as a percentage. Heat release may be based on the LHV (Lower Heating Value) of the fuel or HHV (Higher Heating Value). Process heaters are usually based on LHV and boilers on HHV. The HHV efficiency is lower than the LHV efficiency by the ratio of the two heating values.

Heat is wasted from a fired heater in two ways:

- with the hot stack gas
- by radiation and convection from the setting

The major loss is by the heat contained in the stack gas. The temperature of the stack gas is determined by the temperature of the incoming process fluid unless an air preheater is used. The closest economical approach to process fluid is about 100°F. If the major process stream is very hot at the inlet, it may be possible to find a colder process stream to pass through the convection section to improve efficiency, provided

plant control, and flexibility are adequately provided for. A more common method of improving efficiency is to generate and/or superheat steam and preheat boiler feed water.

The lowest stack temperature that can be used is determined by the dew point of the stack gases. Figures 18.49 and 18.50 may be used to estimate flue gas heat loss.

The loss to flue gas is expressed as a percentage of the total heat of combustion available from the fuel. These figures also show the effect of excess air on efficiency. Typically excess air for efficiency guarantees is 20% when firing fuel gas and 30% when firing oil.

Heat loss from the setting, called radiation loss, is about $1\frac{1}{2}$–2% of the heat release.

The range of efficiencies is approximately as follows:

Very high — 90%+. Large boilers and process heaters with air preheaters.
High — 85%. Large heaters with low process inlet temperatures and/or air preheaters.
Usual — 70–80%.
Low — 60% and less. All radiant.

More detailed discussion on this subject is given in Chapter 18 of this Handbook.

Heat exchangers

Heat exchange is the science that deals with the rate of heat transfer between hot and cold bodies. There are three methods of heat transfer, they are:

- Conduction
- Convection
- Radiation

In a heat exchanger heat is transferred by conduction and convection with conduction usually being the limiting factor. The equipment used in heat exchanger service is designed specifically for the duty required of it. That is, heat exchange equipment cannot be purchased as a stock item for a service but has to be designed for that service.

The types of heat exchange equipment used in the process industry and their selection for use are as follows:

The shell and tube exchanger. This is the type of exchanger most commonly used in a process plant. It consists of a bundle of tubes encased in a shell. It is inexpensive and

is easy to clean and maintain. There are several types of shell and tube exchangers and some of these have removable bundles for easier cleaning. The shell and tube exchanger has a wide variety of service that it is normally used for. These include vapor condensation (condensers), process liquid cooling (coolers), exchange of heat between two process streams (heat exchangers), and reboilers (boiling in fractionator service).

The double pipe exchanger. A double pipe exchanger consists of a pipe within a pipe. One of the fluid streams flows through the inner pipe while the other flows through the annular space between the pipes. The exchanger can be dismantled very easily and therefore be easily cleaned. The double pipe exchanger is used for very small process units or where the fluids are extremely fouling. Either true concurrent or countercurrent flows can be obtained but because the cost per square foot is relatively high it can only be justified for special applications.

Extended surface or fin tubes. This type of exchanger is similar to the double pipe but the inner pipe is grooved or has longitudinal fins on its outside surface. Its most common use is in the service where one of the fluids has a high resistance to heat transfer and the other fluid has a low resistance to heat transfer. It can rarely be justified if the equivalent surface area of a shell and tube exchanger is greater than 200–300 sqft.

Finned air coolers. These are the more common type of air coolers used in the process industry. In a great many applications and geographic areas they have considerable economic advantage over the conventional water cooling. Indeed today it is uncommon to see process plants of any reasonable size without air coolers.

Air coolers consist of a fan and one or more heat transfer sections mounted on a frame. In most cases these sections consist of finned tubes through which the hot fluid passes. The fan located either above or below the tube section induces or forces air around the tubes of the section.

The selection of air coolers over shell and tube is one of cost. Usually air coolers find favor in condensing fractionator overheads to temperatures of about 90–100°F and process liquid product streams to storage temperatures. Air coolers are widely used in most areas of the world where ambient air temperatures are mostly below 90°F. At atmospheric temperatures above 100°F humidifiers are incorporated into the cooler design and operation. The cost under these circumstances is greatly increased and their use is often not justified.

In very cold climates the air temperature around the tubes is controlled to avoid the skin temperature of the fluid being cooled falling below a freezing criteria or in the case of petroleum products its pour point. This control is achieved by louvers installed

to recirculate the air flow or by varying the quantity of air flow by changing the fan pitch.

Box coolers. These are the simplest form of heat exchange. However, they are generally less efficient, more costly and require a large area of the plant plot. They consist of a single coil or "worm" submerged in a bath of cold water. The fluid flows through the coil to be cooled by the water surrounding it. The box cooler found use in the older petroleum refineries for cooling heavy residuum to storage temperatures. Modern day practice is to use a tempered water system where the heavy oil is cooled on the shell side of a shell and tube exchanger against water at a controlled temperature flowing in the tube side. The water is recycled through an air cooler to control its temperature to a level which will not cause the skin temperature of the oil in the shell and tube exchanger to fall below its pour point.

Direct contact condensers. In this exchanger the process vapor to be condensed comes into direct contact with the cooling medium (usually water). This contact is made in a packed section of a small tower. The most common use for this type of condenser is in vacuum producing equipment. Here the vapor and motive steam for each ejector stage is condensed in a packed direct contact condenser. This type has a low pressure drop which is essential for the vacuum producing process.

Details of these heat exchange equipment are given in Chapter 18 of this Handbook.

Basic heat transfer equations. The following equations define the basic heat transfer relationships.

These equations are used to determine the overall surface area required for the transfer of heat from a hot source to a cold source.

The overall heat transfer equation;
The principal equation for heat transfer is given as:

$$Q = UA\,(\Delta t_m)$$

where

Q = Heat transferred in Btu/hr
U = Overall heat transfer coefficient, Btu/hr/sqft/°F
A = Heat transfer surface area sqft.
Δt_m = Corrected log mean temperature difference °F

The overall heat transfer coefficient U is defined by the expression:

$$\frac{1}{U_o} = \frac{1}{h_o} + \frac{1}{h_i} \times \frac{A_o}{A_i} + \frac{1}{h_w} + (rf)_o + (rf)_i \times \frac{A_o}{A_i}$$

where

U_o = overall heat transfer coefficient based on outside tube surface, in Btu/hr/sqft/°F.
h = The film coefficient in Btu/hr/sqft/°F.
r_f = fouling factors in $\frac{1}{\text{Btu/hr/sqft/°F}}$
h_w = Heat transfer rate through tube wall in Btu/hr/sqft/°F.
A = Surface area in sqft

subscripts "o" and "i" refer to outside surface and inside surface, respectively.

Flow arrangements. The two more common flow paths are concurrent and countercurrent. In concurrent flow both the hot fluid and the cold fluid flow in the same direction. This is the least desirable of the flow arrangement and is only used in those chemical processes where there is a danger of the cooling fluid congealing, subliming, or crystallizing at near ambient temperatures.

Countercurrent flow is the most desirable arrangement. Here the hot fluid enters at one end of the exchanger and the cold fluid enters at the opposite end. The streams flow in opposite directions to one another. This arrangement allows the two streams exit temperatures to approach one another.

Logarithmic mean temperature difference Δt_m. In either countercurrent or concurrent flow arrangement the log mean temperature difference used in the overall heat transfer equation is determined by the following expression:

$$\Delta t_m = \frac{\Delta t_1 - \Delta t_2}{\log_e \left[\frac{\Delta t_1}{\Delta t_2}\right]}$$

The Δt's are the temperature differences at each end of the exchanger and Δt_1 is the larger of the two. In true countercurrent flow the Δt_m calculated can be used directly in the overall heat transfer equation. However such a situation is not common and true countercurrent flow rarely exists. Therefore a correction factor needs to be applied to arrive at the correct Δt_m. These are given in Figure 18.A.1 in the appendix to Chapter 9. Details of the shell and tube exchangers including the following:

- Choice of tube side or shell side fluid
- Calculation methods
- Shell and tube baffling
- Types of shell and tube exchangers (fixed sheet, floating head etc.)

are also given in Chapter 18.

Air coolers and condensers. Air cooling of process streams or condensing of process vapors is more widely used in the process industry than cooling or condensing by

exchange with cooling water. The use of individual air coolers for process streams using modern design techniques has economized in plant area required. It has also made obsolete those large cooling towers and ponds associated with product cooling.

As in the case for shell and tube exchangers there are many excellent computer programs that can be used for the design of air coolers. A method given in Chapter 9 for such calculation may be used in the absence of a computer program or for a good estimate of a unit.

A general description and diagrams of the two types of air coolers which are forced air flow and induced air flow has already been given under item “Air Coolers” earlier in this part of the Handbook.

Thermal rating. Thermal rating of an air cooler is similar in some respects to that for a shell and tube described in the previous item. The basic energy equation

$$Q = U\ \Delta T\ A$$

is used to determine the surface area required. The calculation for U is different in that it requires the calculation for the air side film coefficient. This film coefficient is usually based on an extended surface area which is formed by adding fins to the bare surface of the tubes. Thermal rating, surface area, fan dimensions, and horsepower are calculation are given in full in Chapter 18 of this Handbook.

Condensers. In petroleum refining and most other chemical process plants vapors are condensed either in the shell side of a shell and tube exchanger, the tube side of an air cooler, or by direct contact with the coolant in a packed tower. By far the most common of these operations are the first two listed. In the case of the shell and tube condenser the condensation may be produced by cooling the vapor by heat exchange with a cold process stream or by water. Air cooling has overtaken the shell and tube condenser in the case of water as coolant in popularity as described in the previous item.

In the design or performance analysis of condensers the procedure for determining thermal rating and surface area is more complex than that for a single phase cooling and heating. In condensers there are three mechanisms to be considered for the rating procedure. These are:

- The resistance to heat transfer of the condensing film
- The resistance to heat transfer of the vapor cooling
- The resistance to heat transfer of the condensate film cooling

Each of these mechanisms is treated separately and along preselected sections of the exchanger. The procedure for determining the last two of the mechanisms follows that described earlier for single phase heat transfer. The following expression is used

to calculate the film coefficient for the condensing vapor:

$$h_c^{.33} = \left[\frac{8.33^3 \times 10^2}{\mu_f}\right]^{0.33} \times k_f \times \frac{Sg_c}{(M_c/L_c \cdot N_s)}$$

where

h_c = Condensing film coefficient.
M_c = Mass condensed in lbs/hr
L_c = Tube length for condensation.
$= \dfrac{A_{zone} \times (L - 0.5)}{A}$
$N_s = 2.08\ N_t^{0.495}$ for triangular pitch.
k_f = Thermal conductivity of condensate at film temperature.
S_g = Specific gravity of condensate.
μ_f = Viscosity of condensate at film temperature in Cps

Again there are many excellent computer programs that calculate condenser thermal ratings, and these of course save the tedium of the manual calculation.

As in the case of the shell and tube exchanger and the air cooler a manual calculation for condensers is described in Chapter 18 of this Handbook. Again this is done to provide some understanding of the data required to size such a unit and its significance in the calculation procedure. Computer aided designs should however be used for these calculations whenever possible.

Heavy oil cracking

Up to the late 1980s feedstock to FCCU were limited by characteristics such as high Conradson carbon and metals. This excluded the processing of the "bottom of the barrel" residues. Indeed, even the processing of vacuum gas oil feeds was limited to

Conradson carbon $<$ 10 wt%
hydrogen content $<$ 11.2 wt%
metals N1 + V $<$ 50 ppm

During the late 1980s significant research and development breakthroughs have produced a catalytic process that can handle residuum feed.

Feed stocks heavier than vacuum gas oil in conventional FCCU tend to increase the production of coke and this in turn deactivates the catalyst. This is mainly the result of:

- A high portion of the feed that does not vaporize. The unvaporized portion quickly cokes on the catalyst choking its active area.

- The presence of high concentrations of polar molecules such as poly-cyclic aromatics and nitrogen compounds. These are absorbed into the catalyst's active area causing instant (but temporary) deactivation.
- Heavy metals contamination that poison the catalyst and affect the selectivity of the cracking process.
- High concentration of poly-naphthenes that dealkylate slowly.

In FCCU that process conventional feedstocks cracking temperature is controlled by the circulation of hot regenerated catalyst. With the heavier feedstocks an increase in Conradson carbon will lead to a larger coke formation. This in turn produces a high regenerated catalyst temperature and heat load. To maintain heat balance therefore catalyst circulation is reduced leading to poor or unsatisfactory performance. Catalyst cooling or feed cooling is used to overcome this high catalyst heat load and to maintain proper circulation.

The extended boiling range of the feed as in the case of residues tends to cause an uneven cracking severity. The lighter molecules in the feed are instantly vaporized on contact with the hot catalyst, and cracking occurs. In the case of the heavier molecules vaporization is not achieved so easily. This contributes to a higher coke deposition with a higher rate of catalyst deactivation. Ideally the whole feed should be instantly vaporized so that a uniform cracking mechanism can commence. The *mix temperature* (which is defined as the theoretical equilibrium temperature between the uncracked vaporized feed and the regenerated catalyst) should be close to the feed dew point temperature. In conventional units this is about 20–30°C above the riser outlet temperature. This can be approximated by the expression:

$$T_M = T_R + 0.1\,\text{Delta}\,H_C$$

where

T_M = the mix temperature
T_R = riser outlet temperature °C
Delta H_C = heat of cracking in kJ/kg

This mix temperature is also slightly dependent on the catalyst temperature.

Cracking severity is affected by poly-cyclic aromatics and nitrogen. This is so because these compounds tend to be absorbed into the catalyst. Rising the mix temperature by increasing the riser temperature reverses the absorption process. Unfortunately, a higher riser temperature leads to undesirable thermal cracking and production of dry gas.

The processing of resid feedstocks therefore requires special techniques to overcome:

- Feed vaporization
- High concentration of polar molecules
- Presence of metals

Some of the techniques developed to meet heavy oil cracking processing are as follows:

- Two stage regeneration
- Riser mixer design and mix temperature control (for rapid vaporization)
- New riser lift technology minimizing the use of steam
- Regen catalyst temperature control (catalyst cooling)
- Catalyst selection for:
  - ➢ Good conversion and yield pattern
  - ➢ Metal resistance
  - ➢ Thermal and hydrothermal resistance
  - ➢ High gasoline RON

Conventional fluid catalytic crackers can be revamped to incorporate the features necessary for heavy oil (residual) cracking.

An important issue in the case of deep oil (residue) cracking is the handling of the high coke lay down and the protection of the catalyst. One technique that limits the severe conditions in regeneration of the spent catalyst is the two stage regeneration. Figure 11.11 in Chapter 11 shows this configuration.

The spent catalyst from the reactor is delivered to the first regenerator. Here the catalyst undergoes a mild oxidation with a limited amount of air. Temperatures in this regeneration remain fairly low around 700–750°C range. From this first regeneration the catalyst is pneumatically conveyed to a second regenerator. Here excess air is used to complete the carbon burn off and temperatures up to 900°C are experienced. The regenerated catalyst leaves this second regeneration to return to the reactor via the riser.

The technology that applies to the two stage regeneration process is innovative in that it achieves burning off the high coke without impairing the catalyst activity. In the first stage the conditions encourage the combustion of most of the hydrogen associated with the coke. A significant amount of the carbon is also burned off under mild condition. These conditions inhibit catalyst deactivation.

All the residual coke is burned off in the second stage with excess air and in a dry atmosphere. All the steam associated with hydrogen combustion and carry over from the reactor has been dispensed within the first stage. The second regenerator is refractory lined and there is no temperature constraint. The catalyst is allowed to come to equilibrium. Even at high regen temperatures under these conditions lower catalyst deactivation is experienced. The two stage regeneration technique leads to a better catalyst regeneration as well as a lower catalyst consumption. Typically the clean catalyst contains less than 0.05 wt% of carbon. This is achieved with an overall lower heat of combustion. Full details of this concept are given in Chapter 11. Since the unit remains in heat balance coke production stays essentially the same. The

circulation rate of catalyst adjusts itself to any changes in coke deposition on the catalyst according to the expressions:

$$\text{coke make} = \text{delta coke} + \text{c/o}$$

and

$$\text{regenerator temperature} = \text{riser temperature} + \text{C} \times \text{delta coke}$$

where

delta coke = difference between the weight fraction of coke on the catalyst before and after regeneration.
c = unit constant (typically 180–230)
c/o = catalyst to oil ratio

In this regard a small circulation of extremely hot catalyst may not be effective as a large circulation of cooler catalyst. It has been found that there is a specific catalyst temperature range that is desirable for a given feed and catalyst system. A unique dense phase catalyst cooling system provides a technique through which the best temperature and heat balance relationship can be maintained.

Consider the enthalpy requirements for a FCC reactor given in the following table:

	Per pound of feed	
	Btu	%
Feed heating/vaporizing	530.0	69.00
Stripping steam enthalpy	5.0	0.65
Feed steam for dispersion	12.7	1.65
Feed water for heat balance	18.4	2.40
Heat of reaction	200.0	26.04
Heat loss	2.0	0.26
Total	768.1	100.00

It can be seen from this table that 69% of the enthalpy contained in the heat input to the reactor is required just to heat and vaporize the feed. The remainder is essentially available for conversion. To improve operation it would be desirable to allow more of the heat available to be used for conversion. The only variable that can be changed to achieve this requirement is the feed inlet enthalpy. That is through preheating the feed. Doing this, however, immediately reduces the catalyst circulation rate to maintain heat balance. This of course has an adverse effect on conversion. The preheating of the feed can, however, be compensated for by cooling the catalyst. Thus the catalyst circulation rate can be retained and in many cases can be increased. Indeed, by careful manipulation of the heat balance the net increase in catalyst circulation rate can be as high as 1 unit cat/oil ratio. The higher equilibrium catalyst activity possible at the lower

regeneration temperature also improves the unit yield pattern. This is demonstrated in the following table:

Feedstock

°API	24.5
Conradson carbon	1.6

Yields

	Without catalyst cooling	With catalyst cooling
H_2S wt%	0.1	0.19
C_2- wt%	3.4	2.00
C_3 LV%	9.9	10.34
C_4 LV%	13.9	14.51
C_5+ (430:EP) LV%	58.2	60.87
LCO (650:EP) LV%	17.1	15.54
CLO LV%	8.6	8.10
Coke wt%	5.9	6.07
Conversion LV%	74.3	76.36

In summary, catalyst cooling will:

- Slightly increase unit coke
- Give a higher plant catalyst activity
- Be able to handle more contaminated feeds
- Improve conversion and unit yield
- Provide better operating flexibility

In residue cracking commercial experience indicates that operations at regenerated catalyst temperatures above 1,350°F result in poor yields with high gas production. Where certain operations require high regenerator temperatures the installation of a catalyst cooler will have a substantial economic incentive. This will be due to improved yields and catalyst consumption.

There are two types of catalyst coolers available. These are shown as Figure 11.14 in Chapter 11. They are:

- The back mix type
- Flow through type

Both coolers are installed into the dense phase section of the regenerator.

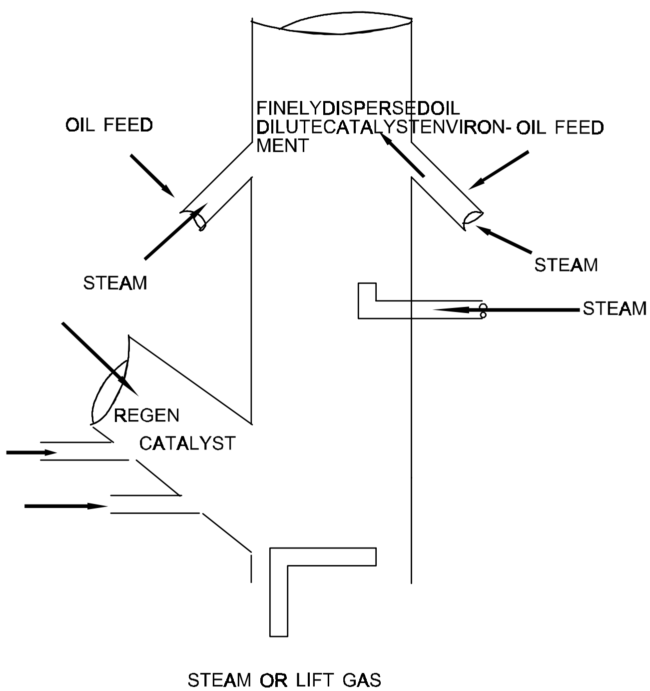
The back mix cooler. Boiler feed water flows tube side in both cooler types. The catalyst in the back mix cooler circulates around the tube bundle on the shell side.

The heat transfer takes place in a dense low velocity region so erosion is minimized. The back mix cooler can remove approximately 50 million Btu's/hr.

The flow through cooler. As the name suggests the catalyst flows once through on the shell side of this cooler. Again erosion is minimized by low velocity operation in the dense phase. This type of cooler is more efficient than the back mix. This unit can achieve heat removal as high as 100 million Btu's per hour.

Mix temperature control and lift gas technology. The equilibrium temperature between the oil feed and the regenerated catalyst must be reached in the shortest possible time. This is required in order to ensure the rapid and homogeneous vaporization of the feed. To ensure this it is necessary to design and install a proper feed injection system. This system should ensure that any catalyst back mixing is eliminated. It should also ensure that all the vaporized feed components are subject to the same cracking severity.

Efficient mixing of the feed finely atomized in small droplets is achieved by contact with a preaccelerated dilute suspension of the regenerated catalyst. Under these conditions feed vaporization takes place almost instantaneously. This configuration is shown in the diagram below:



The regen catalyst stream from the regenerator is accelerated by steam or lift gas injection to move up the riser. The oil feed is introduced atomized by steam into the catalyst environment. The main motive steam into the riser is introduced below the feed inlet point. Good mixing occurs in this section with maximum contact between oil, catalyst, and the steam.

In residue cracking the proper selection of catalyst enables even the most bulky molecules to reach the active catalyst zone. Such zeolite catalyst have a high silica to alumna ratio which cracks the heavy molecules into sizes that can enter the active zone.

Efficient mixing of the catalyst and feed together with the catalyst selection ensures:

- Rapid vaporization of the oil
- Uniform cracking severity of the oil

Another problem that is met within residue cracking is the possibility of the heavier portion of the oil being below its dew point. The presence of poly-cyclic aromatics also affects cracking severity. Increasing the mix temperature to the riser temperature reverses the effect of poly-cyclic aromatics. In so doing, however, thermal cracking occurs which is undesirable. To solve this problem it is necessary to be able to control riser temperature independently of mix temperature. Mix Temperature Control (MTC) is achieved by injecting a suitable heavy cycle oil stream into the riser above the oil feed injection point. This essentially separates the riser into two reaction zones. The first is between the feed injection and the cycle oil inlet. This zone is characterized by a high mix temperature, a high catalyst to oil ratio and a very short contact time.

The second zone above the cycle oil inlet operates under more conventional catalytic cracking conditions. The riser temperature is maintained independently by the introduction of the regenerated catalyst. Thus an increase in cycle oil leads to a decrease in riser temperature, which introduces more catalyst, increases the mix temperature, and the catalyst to oil ratio, and decreases the regenerator temperature.

The lift gas technology. As described earlier it is highly desirable to achieve good catalyst / oil mixing as early and as quickly as possible. The method described to achieve this requires the preacceleration and dilution of the catalyst stream. Traditionally steam was the medium used to maintain catalyst bed fluidity and movement in the riser. Steam, however, has deleterious effects on the very hot catalyst that is used in residue cracking processes. Steam under these conditions causes hydrothermal deactivation of the catalyst.

Much work has been done in reducing the use of steam in contact with the hot catalyst. Some of the results of the work showed that if the partial pressure of steam is kept low, the hydrothermal effects are greatly reduced, in the case of relatively metal free catalyst. A more important result of the work showed that light hydrocarbons imparted favorable conditioning effects to the freshly regenerated catalyst. This was even more pronounced in catalysts that were heavily contaminated with metals.

Light hydrocarbon gases have been introduced in several heavy oil crackers since 1985. They have operated either with lift gas alone or mixed with steam. The limitations to the use of lift gas rests on the ability of downstream units to handle the additional gas. The following table compares the effect of lift gas in resid operation with the use of steam.

Feed: Atmospheric residue 4.3 wt% con carb.

Product distribution	Lift gas	Steam
C_2- wt%	3.2	4.0
C_3/C_4 LV%	11.4/15.1	11.6/15.4
C_5-Gasoline LV%	56, 9	55, 0
LCO + Slurry LV%	23, 9	24, 4
Total C_3 + LV%	107, 3	106, 4
Coke wt%	8, 6	8, 5
H_2 SCFB	70	89
H_2/C_1 Mol	0, 74	0, 85
Catalyst		
Material	←same	same→
*SA, M_2/G	91	90
Ni + V WT ppm	7, 100	7, 300

*SA—surface area of equilibrium FCC catalyst, M_2/Gram.

As can be seen the use of lift gas as an alternative to steam gives:

- Lower hydrogen production
- Lower hydrogen/methane ratio
- Increase in liquid yield

Hot and cold flash separators

Hot and cold flash separation are used in high pressure, high temperature hydro cracking processes. The principal purpose is to recover high purity hydrogen for recycle in as economically a manner as possible. Secondly, as the high temperature

and pressure cracker effluent is to be further processed, it is desirable to route the flashed liquid at as high a temperature as possible to the subsequent process unit.

Figure 11.15 of Chapter 11 of this Handbook shows the general configuration of a residue hydrocracker and visbreaking combination unit.

Bitumen feed from a crude vacuum distillation unit enters the reaction section of the hydro-cracker to be preheated by hot flash vapors in a shell and tube exchanger. A recycle and make up hydrogen stream is similarly heated by exchange with hot flash vapors. The hydrogen stream is mixed with the hot bitumen stream before entering the hydro-cracker heater. The feed streams are risen to the reactor temperature in the heater and leave to enter the top of the reactor vessel. The feed streams flow downwards through the catalyst beds contained in the reactor. Additional cold hydrogen is injected at various sections of the reactor to provide temperature control as the hydro-cracking process is exothermal.

The reactor effluent leaves the reactor to enter a hot flash drum. Here the heavy bituminous portion of the effluent leaves from the bottom of the drum while the lighter oil and gas phase leaves as a vapor from the top of the drum. This vapor is subsequently cooled by heat exchange with the feed and further cooled and partially condensed by an air cooler. This cooled stream then enters a cold separator operating at a pressure only slightly lower than that of the reactor. A rich hydrogen gas stream is removed from this drum to be amine treated and returned as recycle gas to the process. The distillate liquid leaves from the bottom of the separator to join a vapor stream from the hot flash surge drum (visbreaker feed surge drum). Both these streams enter the cold flash drum which operates at a much lower pressure than the upstream equipment. A gas stream is removed from the drum to be routed to the absorber in a distillate hydro-cracking unit. The liquid distillate from the drum is routed to the de-butanizer in the distillate hydro-cracking unit.

The visbreaker section of the unit takes as feed the heavy bituminous liquid from the hot flash drum. This enters the visbreaker furnace via a surge drum. The visbreaker heater has two parallel coils. The oil feed enters these coils to be thermally cracked to form some lighter products. The stream leaving the heater is quenched before entering a flash chamber. This vessel contains some baffled trays and a light gas and oil vapor stream leaves overhead. This stream is subsequently cooled and the distillate formed routed to the cold flash drum. The bottoms from the flash chamber may be fed to a visbreaker vacuum distillation unit where vacuum gas oil can be removed as feed to a fluid catalytic cracker unit. Alternatively this bottom product may be simply routed to an asphalt plant for suitable feed to an asphalt air blower or simple blended with cut-back material for marketable asphalt. Full details of this subject including the development of flashed stream compositions are given in Chapter 11.

Hydraulic analysis of process systems

This item deals with calculating a pressure profile of a process system. Such a calculation is used to size pipelines and to determine the pumping requirements for the system. The following calculation is an example of a typical system process engineers encounter in a design of a plant or in checking out an operating plant's process flow. The attached diagram H5 is used as the basis for this example.

Example calculation

$$\begin{aligned}
\text{Total flow to P-103 A\&B} &= 519{,}904 \text{ lbs/hr} \\
\text{API gravity} = 20.7 &= \text{Sg of } 0.930 \text{ @ } 60^\circ\text{F} \\
\text{Stream temperature} &= 545^\circ\text{F} \\
\text{Sg @ } 545^\circ\text{F} = 0.755 &= 6.287 \text{ lbs/gallon.} \\
\text{Gallons/min @ stream temp} &= \frac{519{,}904}{6.287 \times 60} \\
&= 1{,}378 \text{ gpm.}
\end{aligned}$$

viscosity of the oil @ 545°F = 1.2 cs
The suction line to P-103 A&B is 10″ sched 40.
From Table 19.A.1 in the Appendix Part 2.
Friction loss in feet /1,000 ft of pipe is 9.3 ft (equivalent to .30 psi/100 ft).

Suction line equivalent length

The following information would normally be obtained from a piping general arrangement drawing (a piping GA). For this calculation this information is fictional:

$$\begin{aligned}
\text{Number of standard elbows in the line} &= 8. \\
\text{Number of gate valves (all open) in the line} &= 3 \\
\text{Total straight length of 10}'' \text{ line} &= 85 \text{ ft.}
\end{aligned}$$

From Figure 19.B.2 in the appendix:

$$\begin{aligned}
\text{The equivalent length for 10}'' \text{ elbows is 22 ft per elbow.} &= 22 \times 8 = 176 \text{ ft.} \\
\text{The equivalent length for 10}'' \text{ gate valves is 5 ft per valve.} &= 5 \times 3 = 15 \text{ ft.} \\
\text{Total equivalent line length: } 85 + 176 + 15 &= 276 \text{ ft.}
\end{aligned}$$

Head loss to pump suction due to friction

$$= \frac{9.30 \times 276}{1{,}000} = 2.57 \text{ ft.}$$

In terms of pounds per square inch this is

$$= \frac{2.57 \times 62.2 \times .755}{144} = 0.83 \text{ psi.}$$

Pump suction pressure

Source pressure at vacuum tower draw off = 15 mmHg
= 0.29 psia

$$\text{Static head} = 45\text{ ft.} = \frac{45 \times 62.2 \times .755}{144}$$
$$= 14.7\text{ psia.}$$
$$\text{line loss} = 0.83\text{ psi}$$

Total pressure at the pump suction flange = 0.29 + 14.7 − 0.83
= 14.21 psia. (which is − 0.49 psig).

Calculating the pressures at the pump discharge

Destination pressure at battery limits = 50 psig.
Temperature of the oil at battery limits = 140°F
Viscosity of the oil @ 140°F = 20 cs
S G of the oil @ 140°F = 0.900; lbs/ gal = 7.495.

From a material balance or from plant data: Flow of oil = 191,121 lbs/hr

$$\text{Flow rate} = \frac{191{,}121}{7.495 \times 60}$$
$$= 425\text{ gpm.}$$

1.0 Line pressure drop from E-109 to battery limits
Equivalent length of line:

Straight line = 126 ft.
Number of elbows = 18 equiv length = 18 × 16 = 288 ft.
Number of gate valves = 6 equiv length = 6 × 3.5 = 21 ft.
Number of TEE's = 1 equiv length = 1 × 30 = 30 ft.
Total equivalent length = 465 ft.

Line to battery limits (BL) is a 6″ schedule 40. Then from Table 19.A.2 loss due to friction is 21.4 ft/ 1,000 ft which is equivalent to 0.83 psi/100 ft.

Then line friction loss is

$$\frac{21.4 \times 465}{1{,}000} = 9.95\text{ ft.}$$

or

$$\frac{9.95 \times 62.2 \times 0.900}{144} = 3.86\,\text{psi.}$$

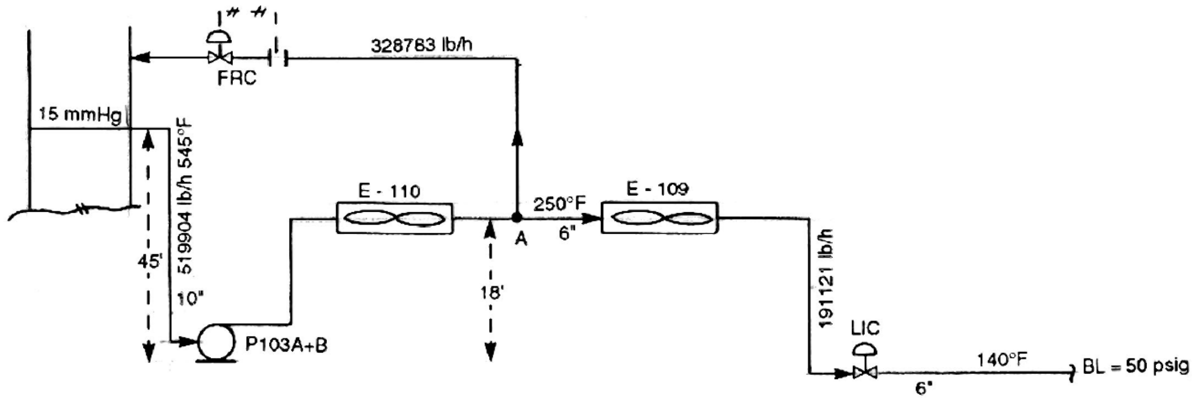


Figure 19.H.1. Example of a system hydraulics.

2.0 Control valve pressure drop

There is a battery limit Level Control Valve (LICV) between E-109 and the BL It is required to calculate the pressure drop for this valve at design flow. The rule of thumb given in Chapter 1.9 will be used to determine this. Thus, the pressure drop will be estimated as 20% of the circuit frictional pressure drop plus 10% of the static head of the receiving vessel.

The oil discharges into a surge drum of another downstream unit. This drum is pressurized by a blanket of inert gas. The net static head to this drum is 15 ft above valve outlet flange. This is equivalent to 6 psi.

The total line pressure drop for the whole circuit is estimated at 3 times that calculated above. (This will be checked and may be revised when the analysis of the whole circuit is complete). This pressure drop therefore is $3 \times 3.86 = 11.58$ psi for line losses. In addition to this line loss there are also two air coolers which have pressure drops as follows:

E-109 = 6 psi (from data sheets).
E-110 = 8 psi

Then total system pressure drop is estimated as:

$$11.58 + 14 = 25.58 \text{ psi.}$$

then control valve pressure drop is:

$$(0.1 \times 6.0) + (0.2 \times 25.58) = 5.2 \text{ psi}$$

3.0 Calculate pressure at point 'A' which is the reflux stream take off

Legnth of line between point 'A' and inlet to E-109 is as follows:

$$\begin{aligned} \text{Straight line} &= 121 \text{ ft} \\ \text{4 Elbows} = 4 \times 16 &= 64 \text{ ft} \\ \text{2 Valves} = 2 \times 3.5 &= 7 \text{ ft} \\ \text{Total 6}'' \text{ sched 40 line equiv} &= 192 \text{ ft} \end{aligned}$$

Temperature of stream at this point is 250°F.

$$\text{Viscosity @ 250°F} = 3.5 \text{ Cs}$$

SG @ 250°F is 0.860 which is 7.16 lbs/gal.

$$\text{Rate of flow into E-109} = \frac{191{,}121}{7.16 \times 60} = 445 \text{ gpm.}$$

Friction loss in 6″ pipe = 16.1 ft/1,000 ft

Total line loss:

$$\frac{192 \times 16.1}{1{,}000} = 3.09 \text{ ft or } 1.15 \text{ psi.}$$

Pressure at point 'A' therefore is the sum of:

$$\begin{aligned}\text{Destination pressure at BL} &= 50 \text{ psig}\\ \text{Pressure drop for E-109} &= 6 \text{ psi}\\ \text{Lossin line from E-109 to battery limits.} &= 3.86 \text{ psi}\end{aligned}$$

$$\begin{aligned}\text{Loss in line from point 'A' to E-109} &= 1.15 \text{ psi}\\ \text{Control valve pressure drop} &= 5.2 \text{ psi}\\ \text{Flow meter (not shown) say} &= 0.2 \text{ psi}\\ \text{Total pressure at point 'A'} &= 66.41 \text{ psig}\end{aligned}$$

4.0 Calculating the pressure at the pump discharge flange

Total flow from the pump is 519,904 lbs/hr

Oil temperature at outlet of E-110 is 250°F.

gpm of flow from E-110 is

$$\frac{519{,}904}{7.16 \times 60} = 1{,}210 \text{ gpm}$$

Line size at this point is 8″ sched 40.
Head loss in this line is 31.1 ft/1,000 ft.

Equivalent length of line:

$$\begin{aligned}\text{Straight line} &= 82 \text{ ft}\\ \text{1 Tee} &= 30 \text{ ft}\\ \text{Total equiv legnth} &= 112 \text{ ft.}\\ \text{Total head loss in line} &= \frac{112 \times 31.1}{1{,}000}\\ &= 3.5 \text{ ft or } 1.3 \text{ psi.}\end{aligned}$$

Pressure at E-110 inlet will be:

$$\begin{aligned}\text{Pressure at point 'A'} &= 66.41 \text{ psig.}\\ \text{Head loss in line} &= 1.3 \text{ psi}\\ \text{Pressure drop across 11-E-10} &= 8 \text{ psi}\\ &= 75.7 \text{ psig}\end{aligned}$$

This pressure is 18 ft above grade as these air coolers are located above the pipe-rack. Allowing 1.5 ft from grade to pump center line, the static head at pump discharge flange is 16.5 ft.

Equivalent length of line from pump to E-110 is:

$$\begin{aligned}
\text{Straight length} &= 155 \text{ ft} \\
12 \text{ elbows} &= 12 \times 20.5 = 246 \text{ ft.} \\
3 \text{ gate valves} &= 3 \times 4.8 = 14.4 \text{ ft} \\
1 \text{ non return valve} &= 1 \times 51 = 51 \text{ ft} \\
\text{Total equivalent length} &= 466.4 \text{ ft}
\end{aligned}$$

Head loss in 8″ sched 40 pipe at a flow rate of 1,378 gpm.
Pump temperature is 545°F
Viscosity at pump temperature is 1.2 Cs
SG at pump temperature is 0.755
Head loss = 28.8 ft/1,000 ft.

$$\begin{aligned}
\text{Total line head loss } &= \frac{28.8 \times 466.4}{1{,}000} \\
&= 13.4 \text{ ft or } 4.38 \text{ psi}
\end{aligned}$$

Then the pump discharge pressure is the sum of:

$$\begin{aligned}
\text{Pressure at E-110 inlet} &= 75.7 \text{ psig} \\
\text{Line pressure drop} &= 4.38 \text{ psi} \\
\text{Static head (16.5 ft)} &= 5.38 \text{ psi} \\
\text{Total discharge pressure} &= 85.46 \text{ psig.}
\end{aligned}$$

5.0 Calculating the pressures in the reflux line from point 'A'

At point 'A' the pressure has been calculated as 66.41 psig.
Flow of the reflux stream (from the material balance) is:

$$519{,}904 - 191{,}121 = 328{,}783 \text{ lbs/hr.}$$

Temperature of the stream is 250°F.

$$\begin{aligned}
\text{Viscosity @ 250°F} &= 3.5 \text{ Cs.} \\
\text{SG @ 250°F} &= 0.860 \text{ and lbs/gal is } 7.16 \\
\text{Rate of flow} &= \frac{328,783}{7.16 \times 60} \\
&= 765 \text{ gpm}
\end{aligned}$$

Line to tower from point 'A' is a 6″ sched 40 and head loss in this line is found to be 40.2 ft/1,000 ft.

Equivalent line lengths:
To the flow controller inlet flange:

$$\begin{aligned}
\text{Straight line} &= 16 \text{ ft} \\
2 \text{ elbows} &= 2 \times 16 = 32 \text{ ft} \\
1 \text{ valve} &= 1 \times 3.5 = 7 \text{ ft} \\
\text{Total equivalent length} &= 81.5 \text{ ft}
\end{aligned}$$

From the flow controller to tower:

$$\begin{aligned} \text{Straight line} &= 71 \text{ ft} \\ 6 \text{ elbows} = 6 \times 16 &= 96 \text{ ft} \\ 1 \text{ valve} = 1 \times 3.5 &= 3.5 \text{ ft} \\ \text{Total equivalent length} &= 171 \text{ ft} \end{aligned}$$

Total line length from point ‘A’ to tower:

$$81.5 + 171 = 252.5 \text{ ft}$$

Total head loss in line due to friction:

$$\frac{252.5 \times 40.2}{1{,}000} = 10.15 \text{ ft or } 3.77 \text{ psi}$$

The pressure required to deliver 765 gpm of reflux to the tower excluding the pressure drop across the control valve at this rate is the sum of the following:

$$\begin{aligned} \text{Destination pressure} &= 0.29 \text{ psia} \\ \text{Static head} &= 14.11 \text{ psi} \\ \text{Distributor (tower internals)} &= 2.0 \text{ psi (from data sheet)} \\ \text{Flow meter pressure} &= 0.5 \text{ psi (from data sheet)} \\ \text{Head loss in line} &= 3.77 \text{ psi} \\ \text{Total required} &= 20.67 \text{ psia} \\ &\quad \text{or } 5.97 \text{ psig} \end{aligned}$$

Then valve pressure drop at design flow of 765 gpm is:

Pressure at point ‘A’—required pressure

$$\begin{aligned} &= 66.41\text{–}5.97 \text{ psig} \\ &= 60.44 \text{ psi} \end{aligned}$$

Note: Line pressure drops are given in Part 2 Appendix B.1.

Hydro-cracking (distillate)

Details of this process are given in Chapter 7. The following section is a description of a typical distillate hydro-cracker having a crude vacuum distillate as feed.

The diagram (Figure 19.H.2) shows a typical hydro-cracking unit in which the fresh feed is pumped through a series of feed/effluent exchangers to the inlet of the first reactor. The preheated feed is mixed with hot recycle gas at the inlet to the first reactor. In this case only the recycle gas passes through the fired heater although in some processes the combined feed and recycle gas are heated. The first reactor is

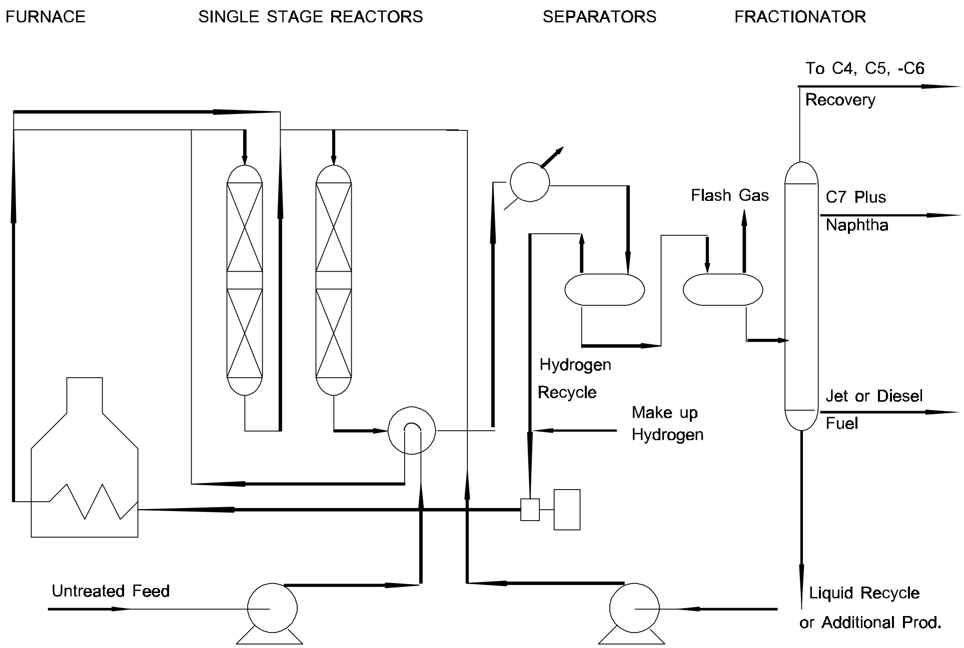


Figure 19.H.2. A distillate hydro cracker.

usually filled with a hydro-treating catalyst for the partial de-sulfurization and de-nitrogenation of the fresh feed. The catalyst employed for the hydro-treating is an alumna based type containing cobalt and molybdenum. To protect the catalyst from fouling by iron compounds and any salt in the feedstock, the first few feet of the reactor is usually used as a guard bed—some processes utilize an external guard reactor.

The hydrogenated feedstock is then mixed with additional hydrogen and passes to the hydro-cracking reactor, where cracking to the desired products takes place. The number of hydro-cracking reactor stages will either be one or two depending upon the products required.

The hydro-cracker reactor effluent is cooled by exchange with fresh feed and recycle hydrogen and is then flashed in the high pressure separator. The liquid from the high pressure separator passes to a further low pressure separator whilst the gas stream, which is rich in hydrogen, is recycled to the reactors. Make up hydrogen is added as required.

The liquid from the low pressure separator is then pumped to the fractionation train where products are separated. The unconverted portion of the fresh feed may then either be recycled for further cracking or used as product. Flash gas from the low

pressure separator is usually treated to remove the acidic components before being sent to the refinery fuel gas system.

Typical feeds include atmospheric and vacuum virgin gas oils, catalytic cycle oils, deasphalted oil, coker gas oil, thermal gas oil, and paraffin raffinates. Heavy feed stocks such as vacuum gas oils are usually limited to an end point of about 1,050°F.

Products range from LPG, naphtha, gasoline through to lube oils; the more usual being naphtha, gasoline, and diesel fuel. It is possible to vary the products from a hydro-cracking unit by merely changing the reactor operating conditions and the fractionation cut point. This flexibility of operation is one of the major factors in favor of hydro-cracking.

The overall hydro-cracking reaction is exothermal. Temperature control of the reactor is accomplished by the introduction of cold hydrogen quench streams at the appropriate locations in the reactor.

The hydro-cracker reactor side

This side of the hydro-cracker is licensed to oil refinery clients. The data requirements therefore are proprietary to the licensor and are provided to clients under the licensing agreement. Use and disclosure of these data are limited to the various clients and/or client's engineering contractor personnel who require such data to design or operate the process.

Operating variables are available to client personnel in the form of graphs or curves. For example and referring to the process diagram H6 some of these would be:

R1 reactor temperature response

- Effect of feed end point and density on required temperature
- Effect of feed nitrogen content on required temperature
- Effect of temperature on R1 product nitrogen content
- Effect of feed rate on required temperature
- Effect of recycle hydrogen purity on required temperature

R2 reactor temperature response

- Effect of feed end point and density on required temperature
- Effect of feed nitrogen content on required temperature
- Effect of R1 product nitrogen on required temperature
- Effect of feed rate on required temperature
- Effect of temperature on conversion to diesel and lighter
- Effect of temperature on diesel/gas oil cut point

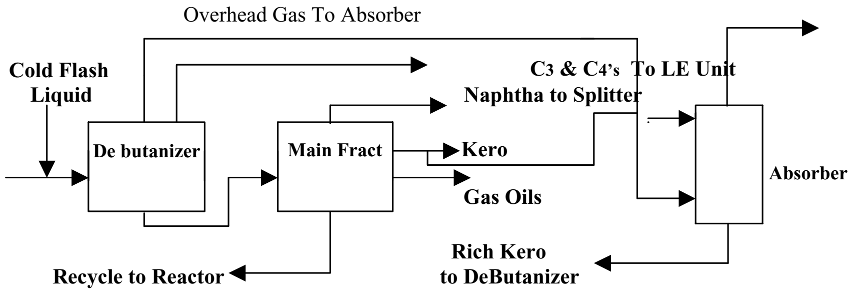


Figure 19.H.3. Block flow diagram of a typical hydro cracker recovery side.

- Effect of recycle hydrogen purity on required temperature
- Effect of gas to oil ratio on required temperature

These curves are made available from the section supervisors as required and under strict security. Discussion on the effect of certain process variables and the mechanism of hydro-cracking are provided in Chapter 7.

Hydro-cracker recovery side

A block flow diagram of a typical hydro-cracker product recovery is given in Figure 19.H.3.

The feed to the main fractionator contains the de-butanized effluent from the hydro-cracker reactor side and the cold flash liquid. The absorber rich liquid is also fed to the de-butanizer. This absorber rich liquid is kerosene saturated with some light gas and most of the propanes and butanes in the de-butanizer overhead gas stream.

The de-butanizer bottom stream is preheated in a fired heater before entering the flash zone of the main fractionator. In this fractionator a full range naphtha stream is taken off overhead. Kero and gas oils are taken off as the two side streams. Kero is stripped by reboiling while the gas oil is steam stripped. A small stream of unconverted oil leaves as the tower bottom product. This is returned to the reactors as recycle.

The ASTM distillation lab data for all streams, together with plant data giving their respective flows are available and can be used to develop a TBP curve for the main fractionator feed. The procedure is given by the following steps:

Step 1. Calculate the TBP curve for light naphtha, heavy naphtha, kero, diesel, and UCO from their respective ATSM distillation data.
Step 2. Plot each of the TBP curves as shown in Figure 19.H.4.
Step 3. Starting with the naphtha divide the TBP curve into about six boiling point fractions.

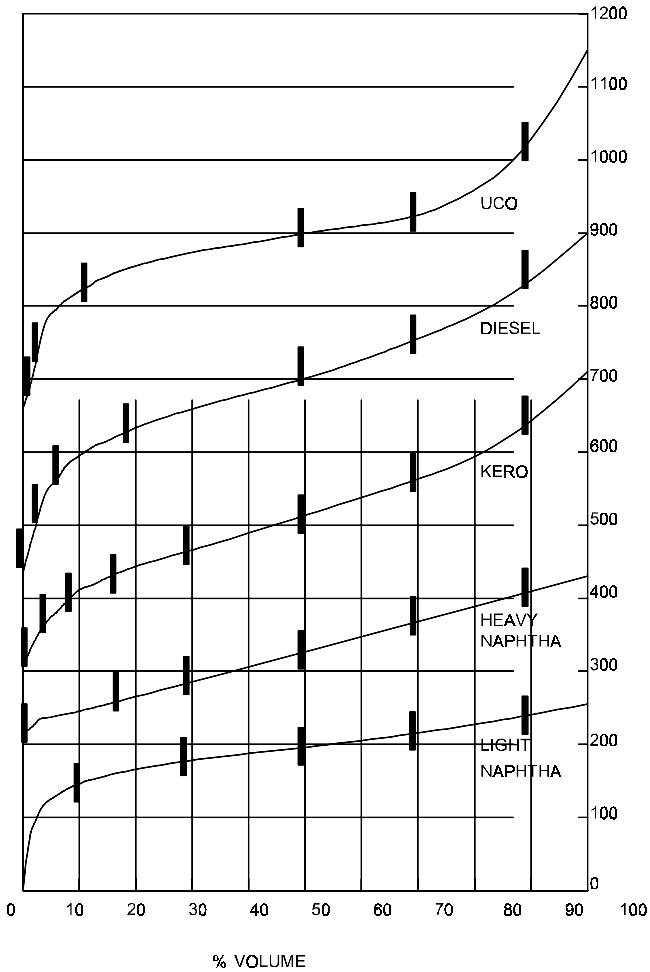


Figure 19.H.4. The TBP of the cuts.

Step 4. Divide the heavy naphtha curve in a smaller manner. In this case, however, the cut points of the fractions in the light naphtha that are also in the heavy naphtha must be identified. These must also be a fraction in the heavy naphtha. For example if the penultimate fraction of the light naphtha has a cut range 220–240°F, and the heavy naphtha starts with a TBP IBP of 220°F, then the first fraction of the heavy naphtha must have an IBP of 240°F.

Step 5. Divide the kero, diesel, and UCO TBP curves in the same manner as the heavy naphtha described in Step 4. Make sure that all common fractions are identified and measured in each product.

Step 6. From the plant flow data calculate the yield of each stream as a volume percent on total feed.

Step 7. List the cut points for each fraction developed in Steps 3 through 5. Against each cut point calculate its percentage on total feed that will be in all 5 product streams. That is, if cut points 180–190°F in light naphtha is 20 vol% on its TBP and light naphtha is 5.06 vol% on total feed then this component with cut range to 180–190°F will be 0.2 g× 5.06 vol% on total feed.

Step 8. Step 8 List the percent of each fraction on feed for all 5 products. Then by adding them horizontally the total of each cut point fraction on total feed is established.

Step 9. Plot the cumulative volume percent from Step 8 against cut point. This is the fractionator feed TBP curve given as Figure 19.H.5.

An example calculation now follow:

Example calculation

The following are lab and plant data from a test run on the recovery of the DHC.

Lab results

	ASTM distillation °F			All converted to D86 °F		
	Light nap	Hy nap	Kero	Diesel	UCO	Total
IBP	27.9	131.5	193.3	261	365.5	
10	79.7	139.2	231.3	324	433	
30	88.8	152.8	247.0	346	447.5	
50	94.1	164.9	264.0	361	455.1	
70	100.7	176.9	283.3	381	463.0	
90	109.2	194.8	317.7	424	510.0	
FBP	114.8	210.3	354.8	455	N/A	
°API	72.6	60.7	46.3	28.3	16.5	
Plant data flows m_3/hr	3.38	13.06	24.74	22.78	2.90	66.86

Calculate liquid TBP curve

LV% Yield

LY naphtha	5.06
HY naphtha	19.53
Kero	37.00
Diesel	34.07
UCO	4.34
Total	100.00

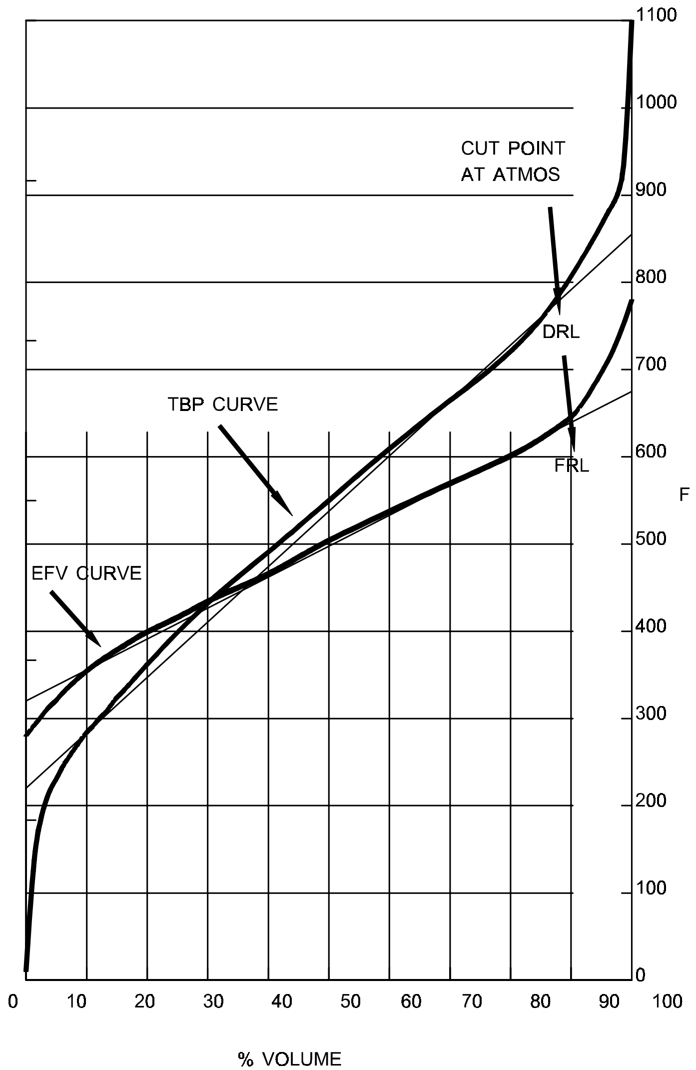


Figure 19.H.5. TBP and EFV curves for the main fractionator feed.

Light naphtha

	ASTM		TBP	
	°F	ΔT	ΔT	°F
IBP	82			12
10	176	94	134	146
30	192	16	32	178
50	201	9	17	195
70	214	13	22	217
90	228	14	20	237
FBP	239	11	14	251

Heavy naphtha

	ASTM		TBP	
	°F	ΔT	ΔT	°F
IBP	270			216
10	282	12	27	243
30	307	25	46	289
50	329	22	37	326
70	351	22	34	360
90	383	32	42	402
FBP	410	27	31	433

Kero

	ASTM		TBP	
	°F	ΔT	ΔT	°F
IBP	379			310
10	448	69	104	414
30	477	29	51	465
50	507	30	47	512
70	541	34	48	560
90	604	63	73	633
FBP	671	67	74	707

Diesel

	ASTM		TBP	
	°F	ΔT	ΔT	°F
IBP	502			439
10	615	113	154	593
30	655	40	65	658
50	682	27	43	701
70	718	36	51	752
90	795	77	85	837
FBP	851	56	61	898

UCO

	ASTM		TBP	
	°F	ΔT	ΔT	°F
IBP	690			662
10	811	121	162	824
30	838	27	49	873
50	851	13	24	897
70	865	14	22	919
90	950	85	93	1012
FBP	00			00

Composite curve for the main fractionator feed

Cut points	% Volume on feed						Cumulative
°F	LT nap	HY nap	Kero	Diesel	UCO	Total	total
12 to 149	0.51					0.51	0.51
to 180	1.01					1.01	1.52
to 190	1.01					1.01	2.53
to 220	1.01					1.01	3.54
to 240	1.01	0.59				1.60	5.14
to 255	0.51	2.72				3.23	8.37
to 285		2.54				2.54	10.91
to 320		3.91	0.37			4.28	15.19
to 365		3.91	1.11			5.02	20.21
to 405		3.91	1.85			5.76	25.97
to 432		1.95	2.59			4.54	30.51
to 465			5.18	0.34		5.52	36.03
to 510			7.40	0.34		7.74	43.77
to 560			7.40	1.36		8.76	52.53
to 635			7.40	4.43		11.83	64.36
to 710			3.70	11.25	0.04	14.99	79.35
to 755				6.13	0.09	6.22	85.57
to 835				6.81	0.39	7.20	92.77
to 900				3.41	1.65	5.06	97.83
to 920					0.87	0.87	98.70
to 1,010					0.87	0.87	99.57
to 1,160					0.43	0.43	100.00
Totals	5.06	19.53	37.00	34.07	4.34	100.00	

Hydrogen

The development of the catalytic reformer and the significant amount of hydrogen provided by the process gave rise to the hydro skimming refinery that is most common

in present day petroleum refining. In this type of refinery the produced reformer hydrogen stream is used as the major component for the following treating processes:

- Hydro-desulfurizing
- Kerosene de-aromatization
- Olefin saturation
- Lube oil de colorization

Details of catalytic reforming are given in Chapter 5 while the major hydro-treating processes are discussed in Chapter 8. The availability of hydrogen from the catalytic reformer continued to support the hydro-skimming refinery comfortably until the development of the hydro-cracker process. The availability of hydrogen from the traditional source of catalytic refining fell far short both in quantity and in sustained purity to satisfy this new process. To overcome this shortfall in refineries whose process configuration included hydro-cracking, Hydrocarbon conversion to hydrogen and CO were installed. The most common of these is the deep conversion of naphtha or light hydrocarbon gases. These processes contained a fired reactor whose tubes contain a catalyst. The feed with a quantity of steam are introduced in this reactor. The hydrocarbon is reduced to its basic components of carbon as CO and hydrogen. A series of shift reactors and a methanation reactor produces the rich hydrogen stream required by the hydro-cracker process. As some sulfur removal is required, this is usually accomplished by traditional means (i.e., amine absorption, or hot potassium carbonate, or in some cases molecular sieves).

Hydro-treating

Naphtha hydro-desulfurization. This uses cat reformer hydrogen or similar on a once through basis. Heavy naphtha feed to the cat reformer is fed to the naphtha hydro-desulfurizer from storage. The feed stream and the hydrogen gas stream are preheated by exchange with the hot reactor effluent stream. The feed then enters the fired heater which brings it up to the reactor temperatures (about 450°F) and leaves the heater to enter the reactor which operates at about 400–450 psig. Sulfur is removed from the hydrocarbon as hydrogen sulfide in this reactor and the reactor effluent is cooled to about 100°F by heat exchange with the feed. The cooled effluent is collected in a flash drum where the light hydrogen rich gas is flashed off. This gas enters the suction side of the booster compressor which delivers it to other hydro-treaters. The liquid phase from the drum is pumped to a reboiled stabilizer. The overhead vapor stream from the stabilizer is routed to fuel while the bottom product, cat reformer feed, is pumped to the cat reformer.

Gas oil hydro-desulfurizer. This process uses a recycled hydrogen stream to de-sulfurize a gas oil feed. The flow sheet, Figure 19.H.6, shows the gas oil feed entering

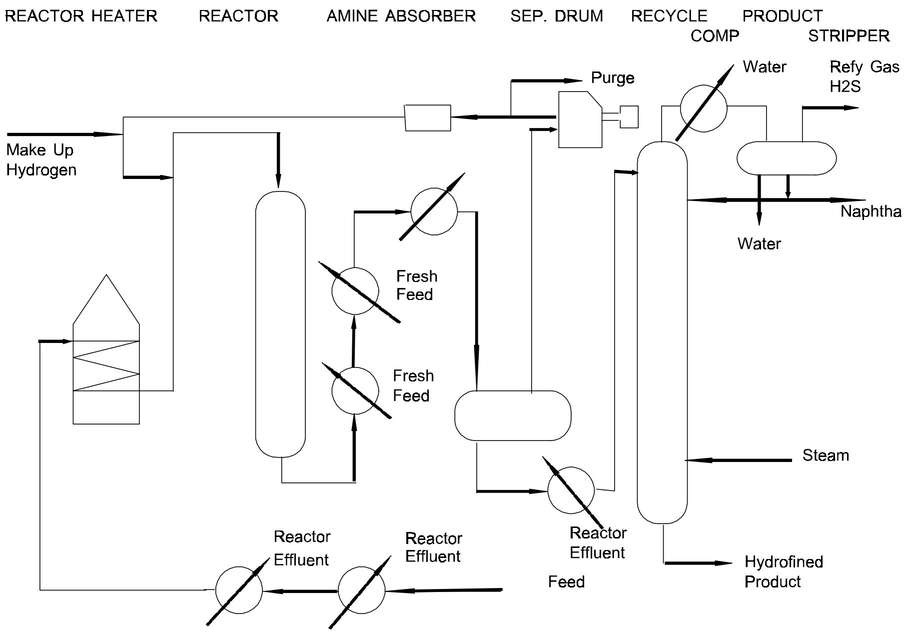


Figure 19.H.6. A typical gas oil hydro de-sulfurizer.

the unit to be preheated with hot effluent stream before entering a fired heater. Its temperature is increased to the reactor temperature of about 750°F in this heater. A hydrogen rich stream is introduced at the coil outlet prior to the mixed streams entering the reactor. The reactor contains a bed of cobalt molybdenum on alumna catalyst and de-sulfurization takes place over the catalyst with 70–75% of the total sulfur in the oil being converted to H_2S.

The reactor effluent is cooled by the cold feed stream, water, or air. This cooled effluent enters a flash drum where the gas phase and liquid phase are separated. The gas phase rich in H_2S and hydrogen enters the recycle compressor. The gas stream then enters an amine contactor where the H_2S is absorbed into the amine and removed from the system. Although the diagram shows a purge stream before the amine absorber in most cases the purge is down stream after the amine cleanup. The purged gas is replaced by fresh hydrogen-rich make up stream thus maintaining the purity of the recycle gas.

The liquid phase leaving the flash drum is preheated before entering a stream stripping column where the light ends created in the process are removed as overhead products. The bottom product leaves the tower to be cooled and stored.

Reactor conditions at start of run. Reactor conditions required for the proper operation of catalytic units are dependent on the type of catalyst used. In hydro-treating therefore reactor side conditions and operation are proprietary to the licensor of the process. However, the following data is an average and does not reflect any particular licensors' process.

The variables for hydro-treater operation are:

- Reactor inlet temperature
- Reactor pressure
- Recycle rate required
- Purity of the inlet hydrogen stream
- Space velocity

These change with the degree of de-sulfurization required, feed cut and quality, and the catalyst age.

There are typical conditions for the reactor side which are in the public domain:

Straight run naphtha de-sulfurization

Reactor inlet temperature	— 650°F.
Reactor pressure	— 500–600 psig
Space velocity v/v/hr	— 4–6
Hydrogen purity at inlet	— 75% mole
Recycle rate scf/bbl	— 500–550

De-sulfurization to < 5 ppm total sulfur.

Diesel de-sulfurization

Reactor temperature	— 650°F
Reactor pressure	— 750–1,000 psig
Space velocity v/v/hr	— 1.5–2
Recycle rate scf/bbl	— 600–700
De-sulfurization:	— remove 85% sulfur in feed.

Hydrogen consumption in these units can be calculated and this depends to a large extent only on feed quality. That is the amount of sulfur (and nitrogen in some cases) and the presence of olefinic material.

Predicting hydrogen consumption in naphtha hydro de-sulfurization

This item describes a method of predicting the hydrogen consumed in hydro-treating straight run naphtha. Emphasis is based on SR naphtha. Treating cracked naphtha and gas oils need approximately three to five times the amount of hydrogen than straight run.

The method for predicting hydrogen consumption now follows with the steps described below:

Step 1. From the naphtha TBP and the assay estimate the weight percent sulfur in the naphtha feed (see Item 1.4).

Step 2. Establish the throughput of the naphtha. Assume the feed will be completely desulfurized in the process.

Step 3. Calculate the moles of sulfur removed by the chemical equation

$$H_2 + S = H_2S$$

Fix the moles of hydrogen required to satisfy the reaction given above. That is moles hydrogen equals moles sulfur removed.

Step 4. Estimate the amount of hydrogen required to saturate the hydrocarbon chain or ring *after* the sulfur molecule is removed. In naphtha fractions the sulfur compounds are relatively simple in structure. A figure of 2 or 3 times the hydrogen used for sulfur removal is reasonable for resaturation. Remember this only applies to straight run feeds.

Step 5. The remaining consumption of hydrogen is to replace the hydrogen lost from the system in solution with the liquid product leaving. This can be a very significant quantity. Calculate using Steps 6 through 10.

Step 6. Establish the component analysis of the make up gas. This is usually catalytic reformer off gas. Calculate the amount in moles/hr of each component that satisfies the chemical reaction quantity calculated in Steps 3 and 4.

Step 7. Let x moles/hr be the hydrogen that leaves in solution with the product. Calculate in terms of x the proportion of the other components related to the hydrogen that also leave in solution with the product. This is each component's moles divided by the hydrogen component and multiplied by x.

Step 8. Add the C_1 through C_5's portion of the make up gas to the x component's calculated in Step 7.

Step 9. The quantity calculated in Step 8 plus the moles of naphtha product is the liquid phase that leaves the separator (i.e., the unstabilized product). By definition this is in equilibrium with the gas phase that leaves the separator drum. Calculate, using the liquid phase composition, its bubble point at the separator drum conditions.

Step 10. Again by definition the y factor calculated in Step 9 (i.e., $y = Kx$) is the composition of the vapor phase leaving the separator drum. As $\Sigma y = \Sigma Kx$ then equate and solve for x as moles hydrogen leaving in solution with the hydro-treated product.

Step 11. The gas phase composition is calculated by substituting the calculate value for x in Step 10. If the unit has a recycle gas stream, this is the composition of the recycle gas.

Step 12. The total hydrogen and hydrogen gas stream make up to the unit can now be completed with the addition of the moles in solution calculated in Step 10.

Predicting the hydrogen consumption in gas oil hydro-treating—with gas purge

Diesel hydro-treating is in many ways similar to naphtha hydro-treating. However, because of a more complex molecular structure in the diesel fraction and more complex sulfur compounds some additional consideration must be made in this case. There will be a higher quantity of sulfur and these will contain disulphides and thiophenes which are complex ring compounds of sulfur. More light ends are made in the process when these compounds are broken to release the sulfur.

Because of the quantity of sulfur released as H_2S there is every probability that the recycle gas will require amine treating to remove this H_2S and thus retain its purity. There is also a need to purge off some of the recycle gas and replace it with fresh catalytic reformer (or high hydrogen content gas). This will be so if the light end is high and the subsequent purity of the recycle gas diminished.

In this item consideration has been given to amine treating and purging the recycle. The purging is an added item to be satisfied by the make up gas consumption. The method of predicting hydrogen consumption and recycle gas purity is given by the following steps:

Step 1. From the feed TBP and assay calculate its sulfur content.

Step 2. Set the degree of de-sulfurization required. This will depend on catalyst and reactor conditions. Most well designed modern diesel hydro-treaters can de-sulfurize heavy gas oil to remove at least 85 wt% of its sulfur content. In the case of automotive diesel, current requirements for ultra-low sulfur diesel (ULSD) are expected to bring sulfur specifications down to <50 ppm. This, however, varies from country to country, with many still in the 300–500 ppm range or even higher.

Step 3. Establish the feed throughput. This will depend on the space velocity required for Step 2.

Step 4. Estimate the light ends produced in the process. This can be done by referring to plant records. As a rule of thumb this can be in the form of C_5+ naphtha at about

6–10% by vol of feed. Some C_5's and lighter are also formed but these are usually in small quantities.

Step 5. As in the method used for naphtha hydro-treating, calculate the hydrogen required to remove the sulfur molecules. Again add 2 times this quantity to saturate the compounds that contained the sulfur.

Step 6. The light ends formed through the minor cracking to release thiophenes and disulfides will need to be saturated. This consumes hydrogen. Approximately 2 moles of hydrogen will be required for this purpose per mole of light ends formed. Using past lab tests on the hydro-treater naphtha develop the TBP and split to pseudo components. Allocate mole weights and gravities to these components to arrive at a number of moles/hr for the light ends. Calculate the hydrogen consumption.

Step 7. The remaining hydrogen requirements will be to replace hydrogen lost in solution with the liquid product and of course that lost in the purge stream. Commence with the calculation to determine solution loss as follows.

Step 8. Establish the component analysis of the make up gas. This is usually catalytic reformer off gas or if the naphtha hydro-treater is operating on a once through gas basis it will be the off gas from that unit.

Step 9. Calculate the amount in moles/hr of each component associated in the make up gas with the hydrogen required for the chemical reactions calculated in Steps 5 and 6.

Step 10. Let x moles/hr be the hydrogen that leaves in solution with the liquid product from the separator and the purge gas. Calculate in terms of x the proportion of the other components in the make up gas associated with the hydrogen.

Step 11. Add the C_1–C_5 portion of the make up gas to the x components calculated in Step 10. Add also the C_5+ naphtha components which were made in the process and of course a guess at the number of moles of H_2S that will be in the liquid phase of the separation drum. To do this look at the "K" (equilibrium constant) for H_2S at drum conditions. Use this to estimate its proportion in liquid. For example if $K = 1$ then the split will be close to 50% in liquid and 50% in vapor.

Step 12. Set the amount of purge in terms of its proportion to the liquid product (that is set the V/L for flash vaporization). This will be such as to provide a recycle gas hydrogen content of above 63% mole after H_2S removal. This figure is trial and error. Start with $V/L = 0.1$.

Step 13. Carry out a flash calculation in terms of x and using V/L set in Step 12. Solve for x. The vapor steam from this calculation is the purge gas in terms of moles/hr and composition. It also is the composition of the recycle gas.

Step 14. Complete the calculation for hydrogen consumption and make up gas using the value for x above.

An example calculation now follows.

Example calculation

Feed to diesel hydro-treater in this case will be heavy gas oil.

$$\begin{aligned}\text{Gas oil cut} &= 610^\circ\text{F} \rightarrow 690^\circ\text{F Kuwait crude}\\ &\quad\text{Mid boiling point } 650^\circ\text{F.}\\ \text{Unit throughput} &= 5{,}500 \text{ BPSD (blocked operation)}\\ \text{From assay sulfur content} &= 2.1 \text{ wt\%}\end{aligned}$$

De-sulfurization shall be 85%.

$$\begin{aligned}\text{lbs/hr gas oil} &= 70{,}078\\ \text{Sulfur in feed} &= 1{,}472 \text{ lbs/hr}\\ \text{Sulfur removed} &= 1{,}251 \text{ lbs/hr}\\ \text{Hydrogen for sulfur removal} &= \frac{1{,}251}{32} = 39 \text{ moles/hr}\end{aligned}$$

7 vol% of C_5+ naphtha is produced in the reaction.

Say this has the following composition:

	Vol%	BPSD	GPH	lbs/hr	MW	Moles/hr
C_6	18.8	72.4	127	702	86	8.2
C_7	23.6	90.9	159	911	100	9.1
C_8	27.1	104.3	183	1077	114	9.4
C_9	13.2	50.8	89	535	128	4.2
$C_{10}+$	17.3	66.6	117	715	142	5.0
	100.0	385	675	3940		35.9

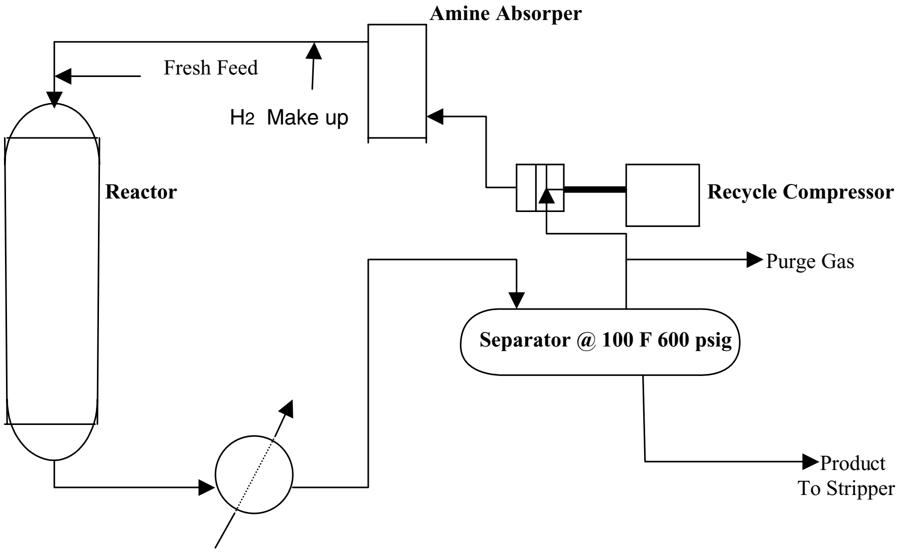
Approximately 2 moles of H_2 per mole will be required to saturate light ends as they are produced.

Then this hydrogen $= 35.9 \times 2 = 71.8$

Then total hydrogen make up will be

$$\begin{aligned}\text{Sulfur removal} &= 39 \text{ moles/hr}\\ \text{Saturating after de-sulfurizing} &= 78 \text{ moles/hr}\\ \text{Light ends} &= 71.8\\ \text{Total} &= 188.8 \text{ moles/hr}\end{aligned}$$

In addition there will be losses out of the system by H_2 in liquid solution and a purge stream. See following diagram



Total make up gas for chemical reaction:

	Mole fract*	Moles/hr
H_2	0.697	188.8
C_1	0.093	25.2
C_2	0.089	24.1
C_3	0.074	20.0
iC_4	0.016	4.3
nC_4	0.020	5.4
iC_5+	0.011	3.0
	1.000	270.8

* From a catalytic reformer.

Let x moles/hr be H_2 in solution lost from the system in liquid solution and purge. Total make up gas then is:

	Consumed in reaction	Loss in solution/purge	Total make up		
H_2	188.8	X	188.8	+	X
C_1	25.2	0.134 X	25.2	+	0.133 X
C_2	24.1	0.128 X	24.1	+	0.128 X
C_3	20.0	0.106 X	20.0	+	0.106 X
iC_4	4.3	0.023 X	4.3	+	0.023 X
nC_4	5.4	0.029 X	5.4	+	0.028 X
C_5+	3.0	0.016 X	3.0	+	0.016 X
	270.8	1.436 X	270.8	+	1.434 X

Set the purge to be 15% mole of liquid to stripper. Thus V/L = 0.15 (1st trial).

Calculate flash for effluent in terms of x at V/L = 0.15. Solve for x. Thus

	x_F effluent	615 PSIK K 100°F	V/L = 0.15 V/L K	V/L = 0.15 $L = \frac{X_F}{1+VLK}$	Liquid to stripper L moles/hr	Purge gas V moles/hr	Recycle gas composition
H_2	x	32	4.8	0.172 x	7.15	34.42	62.85
C_1	25.2 + 0.133 x	3.8	0.51	16.05 + 0.085 x	19.58	11.15	20.36
C_2	24.1 + 0.128 x	1.2	0.18	20.42 + 0.108 x	24.91	4.51	8.23
H_2S	19.0	1.0	0.15	16.52	16.52	2.48	4.53
C_3	20.0 + 0.106 x	0.5	0.075	18.60 + 0.099 x	22.72	1.69	3.09
iC_4	4.3 + 0.023 x	0.25	0.0375	4.14 + 0.022 x	5.05	0.21	0.38
nC_4	5.4 + 0.028 x	0.19	0.0285	5.25 + 0.027 x	6.37	0.19	0.35
C_5	3.0 + 0.016 x	0.085	0.0128	2.96 + 0.016 x	3.63	0.04	0.07
C_6	8.2	0.044	0.0066	8.15	8.15	0.05	0.09
C_7	9.1	0.020	0.0030	9.07	9.07	0.03	0.05
Oil	242	–		242	242	Nil	–
Total	360.3 + 1.434 x			343.16 + 0.529 x	365.15	54.77	100.00

$$\frac{(360.3 + 1.434\,x) - (343.16 + 0.529\,x)}{(343.16 + 0.529\,x)} = 0.15$$

$$17.14 + 0.905\,x = 51.474 + 0.0794\,x$$

$$x = \frac{34.334}{0.826} = 41.57 \text{ moles/hr.}$$

Substituting in the table above total effluent (less recycle) = 419.92 moles/hr.

The recycle gas H_2 content will be 62.9 mole% before H_2S removal.

If there is an amine contactor in the system H_2 purity of the gas becomes 65.8 mole%, which is quite good. This gave a purge steam of 36.59 moles/hr.

And the recycle gas purity was 61.2 mole% with no H_2S removal. With H_2S removal this became 64.2 mole%, which is borderline.

Total hydrogen to the plant at a purge ratio of 0.15 will be:

Sulfur removal	= 39 moles/hr
Saturating	= 78 moles/hr
Light ends	= 71.8 moles/hr
Hydrogen in liquid	= 7.2 moles/hr
Hydrogen in purge	= 34.4 moles/hr
	= 230.4 moles/hr

$$\text{Make up gas stream from catalytic reformer} = \frac{230.4}{0.697} = 330.5 \text{ moles/hr}$$

or 545 SCF/136L of fresh feed

Estimating the hydrogen consumption for olefin separation

This item gives a simple method for estimating the hydrogen consumption when treating cracked stocks. This method uses the correlation

$$\text{BR number} = \frac{\text{Percent olefins} \times 160}{\text{MW olefins}}$$

Where BR number is the bromine number of the stock. This can be obtained by lab analysis. The mole weight of the olefins is estimated as 1.3 times the mole weight of the paraffin with the same mid boiling point of the cut.

The hydrogen consumption for saturation is taken at 6.5–8.0 SCF hydrogen per barrel for every unit of bromine number reduction that occurs in the process. Bromine reduction in hydro-treating is estimated as follows

LT cracked naphtha	— 90–100% reduction
FCCU cycle oil	— 12 unit reduction
Coker gas oil	— 40 unit reduction
Visbreaker gas oil	— 40–45 unit reduction

Use 6.5 SCF/Bbl per bromine unit reduction for naphtha and light oil and 8.0 for the heavier feeds.

A sample calculation now follows:

Example calculation

Consider a cracked naphtha 180–380°F cut

API = 51.0
% S = 0.89

Pona analysis given 30% olefins by vol.

Calculate bromine number from the following.

$$\text{BR no.} = \frac{\%\,\text{olefins} \times 160}{\text{MW olefins}}$$

Mole wt of Olefins 1.3 times mole weight paraffin with same boiling point as the Cuts mid BPT.

$$\begin{aligned}\text{In this case mid BPT is } 200^\circ\text{F} &= \text{Heptane } C_7 \text{ Mole wt } 100\\ \text{Olefin mole wt} &= 130\\ \text{Then bromine no.} &= \frac{30 \times 160}{130} = 37\end{aligned}$$

Olefin saturation is 6.5 SCF hydrogen/Bbl per unit of bromine number reduction. With naphtha this is usually about 95%.

$$\begin{aligned}\text{Then hydrogen required} &= 6.5 \times 37 \times 0.95 \text{ SCF/Bbl}\\ &= 228.5 \text{ SCF/Bbl of Feed}\end{aligned}$$

Further details including reaction mechanism of hydro-treating are discussed and described in Chapter 7 of this Handbook.

I

i-component

The "i" as a prefix to a chemical component indicates that the compound is an isomer. There are several isomers in petroleum refining and the most common relate to the light components of the structure. Notably these are:

iso-Butane—iC_4
iso-Pentane—iC_5
iso-Hexane—iC_6

and so on through the homologue. When isomers exist and are quoted together with the normal compound this normal compound will be identified by a prefix n.

Impeller speeds (pumps)

Two types of centrifugal pumps are used in petroleum refining. One at an impeller speed of 3,550 rpm and the other type operating at an impeller speed of 2,950 rpm. Some difference in their operating characterization are given in Table 19.I.1.

In general, centrifugal pumps should not be operated continuously at flows less than approximately 20% of the normal rating of the pump. The normal rating for the pump is the capacity corresponding to the maximum efficiency point. The table lists the minimum desirable flow rates which should be maintained by continuous re-circulation, if the required process flow conditions are of lower magnitude: Care must be exercised in the design of any re-circulation system to insure that the re-circulated flow does not increase the temperature of pump suction and cause increased vapor pressure and reduction of available NPSH.

For low head pumps that can operate at 1,750 or 1,450 rpm, the above normal and minimum continuous capacities are reduced by 50%. Pump details, description and discussion are given in Chapter 18.

Table 19.I.1. Impeller speed characteristics

		60 Cycle Speed (3,550 rpm)	
Head range feet	Pump type	Minimum continuous capacity rating GPM	Normal rating of pump GPM
To 100	1 stg	10	60
100–350	1 stg	15	75–100
350–650	2 stg	30	150
650–1,100	2 stg	40	160
400–1,200	Multistg	15	50
1,200–5,500	Multistg	40	100–120
50 Cycle speed (2,950 rpm)			
To 75	1 stg	10	50
75–250	1 stg	15	60–80
250–450	2 stg	25	120
450–775	2 stg	30	130
250–850	Multistg	10	40
850–3,800	Multistg	30	80–100

Table 19.I.2. Example of viscosity blending

Component	Vol%	Mid BPt °F	Viscosity Cs 100°F	Blending index	Viscosity factor
	(A)			(B)	(A × B)
1	13.0	410	1.49	63.5	825.5
2	16.5	460	2.0	58.0	957
3	21.0	489	2.4	55.0	1,155
4	18.0	520	2.9	52.5	945
5	18.5	550	3.7	49.0	906.5
6	13.0	592	4.8	46.0	598
Total	100.0				5,387.0

$$\text{Overall viscosity index} = \frac{5{,}387}{100} = 53.87$$

From Figure 1.8 an index of 53.87 = 2.65 Cs
(Actual plant test data was 2.7 Cs)

Indices

Indices are used extensively in petroleum refining technology to correlate one set of data with another. Chapters 1 and 3 provide indices that relate the properties of various components to temperature, viscosities, flash point blending and the like. A number of these indices are used in the blending of petroleum fraction to give the properties of the blended product. For example, the components listed in Table 19.I.2 are to be blended in the proportions given and the viscosity of the blended product determined.

Initial boiling points

Initial boiling points or IBP's refer to the temperature at which a petroleum cut begins to boil. Usually this temperature is taken as that at atmospheric pressure. These are determined in the refinery's laboratory from the ASTM distillation carried out as a routine test. Details of these tests are given in Chapter 7. Briefly the initial boiling point is the temperature of the boiling liquid vapor whose first condensate drop enters the measuring cylinder at the condenser outlet. The IBP of the TBP curve is usually calculated from the ASTM test results in the refinery. TBP curves are not usually part of the refinery test schedules but belong to the company's research and development center. A similar comment applies also to the EFV curve. See Chapter 3 for the calculation of TBP and EFV curves. The final boiling point of the ASTM distillation test is the maximum temperature noted after the boiling flask has boiled dry. Sometimes the final boiling point (FBP) is called the ASTM end point.

Instrumentation

The proper operation and performance of any process depends as much on a properly designed control system and its supporting instruments as the correct design and specification of the equipment contained in the process.

Control systems in a process are aimed at maintaining the correct conditions of Flow, Temperature, Pressure, and Levels in process equipment and piping. These are described and discussed in detail in Chapter 13. The system covers four major types of controls which are:

- Flow control
- Temperature control
- Pressure control
- Level control

The principal objective of all these types of controls is to maintain a steady stable plant operation and to enable changes and emergencies to be handled safely. The system must also be designed to ensure that any process changes can be accommodated with minimum risk of damage to plant equipment. The instruments that support the plant control system are gauges and control valves. Not all gauges have a control function; many are for plant performance record or for indication only, for example a pressure gauge on a pump discharge is there to indicate that the pump is operating correctly. A flow gauge in the line as orifice plate assembly indicates the flow quantity (usually on a control room chart) and sets an associated control valve action. In the petroleum refinery the major instruments are:

Flow	— Orifice assembly
Temperature	— Thermocouples
Pressure	— Bourdon tube gauge, differential pressure
Level	— Float type, displacer, or differential pressure type

The addition of ‘on stream’ analyzers constitutes a major instrument system, particularly if the refinery operates on automated control. This is standard practice in all major refineries.

Internals (Vessels)

The purpose of vessel internals may be characterized as follows:

- To enhance heat and mass transfer (e.g., fractionating towers)
- To maintain proper residence time for settling (e.g., condensate drums)
- To promote good distribution of fluids (vessel inlet distributors)
- To prevent vortexing of fluids leaving vessels to pump suction

A brief description of each of the vessel internals are as follows:

Heat and mass transfer is required in the operation of distillation fractionators. These include steam (or inert gas) strippers. The method used to achieve this is to fit a tower with fractionating trays. With the use of a reboiler supplying heat to the tower botton and cold reflux stream introduced at the tower top heat and mass transfer occurs successively on these trays. Full details, discussion and examples are given in Chapters 3–12. For the same purpose of heat and mass transfer the trays may be replaced with a packing, again this is described in Chapter 3 and Chapter 18. These internals are also used where mass transfer only is required (e.g., some absorber units, and liquid/liquid extraction units).

A number of vessels in petroleum refining are used to collect and separate immiscible fluids. The most common are fractionator overhead distillate drums. In many cases the fluid entering the drum is a mixture of hydrocarbon and water. In these cases it is necessary to retain the mixed fluid in the drum until the phases separate out. A baffle arrangement is used for this purpose slowing the fluid flow from the drum inlet to outlet meeting the required residence time.

In many processes, particularly those that utilize trays or packing it is important that the fluid entering is evenly distributed over the tray or the packing surface. This is achieved by a carefully designed distributor pipe with slots or holes. In large packed towers there may be several rigs of sprays covering the packing surface. In the case of drums the fluid entering is impinged on a horizontal plate to effect a curtain of the fluid entering the body of the drum. This enhances the separation of any vapor that the fluid contains and separates the two phases. Most fractionator overhead condenser drums are fitted with these 'Splash Plates'.

All vessels whose outlet nozzles feed directly to pump suction are fitted with a vortex breaker. This is simply a plate placed directly above the outlet nozzle in the vessel. The plate is supported by legs keeping it above the nozzle itself. This breaks down any vortex that may tend to form owing to the velocity of the fluid being drawn into the pump suction.

Investment analysis

(See earlier item on economic analysis) Refer also to Chapter 17.

Isomerization

The primary commercial use of the branched isomers of C_4, C_5, and C_6 paraffins is in the production of clean-burning, high-performance transportation fuels. The elimination of tetraethyl lead over the last 30 years as a means of improving the

antiknock properties of gasoline and more-recent regulations restricting motor fuel composition have led refiners to select alternative means of producing high-quality gasoline, (see also Chapter 2). As a result of benzene concentration restrictions, end-point and olefin content limitations, and potential limitations on total aromatics concentration, the choices of high-quality gasoline blending components available in the typical refinery are limited. Isomerate, the gasoline blending component from light paraffin isomerization, is an ideal choice. Another equally valuable blending components is alkylate resulting primarily from the acid-catalyzed reaction of iso-butene with an aliphatic olefin. Both isomerization and alkylation yield highly branched, high-octane paraffinic blending components that by themselves can satisfy the strictest environmental requirements. Often, n-butane isomerization is one of the sources for the iso-butane requirements in alkylation.

The process flow for a typical isomerization plant is give below as Figure 19.I.1.

The naphtha feed is pre-heated by the reactor effluent before entering the isomerization reactor. The feed mixed with the hydrogen stream flows down the reactor through the catalyst bed. The isomerization reaction takes place in the catalyst bed and the reactor effluent leaves the bottom of the reactor to be cooled first by heat exchange with the incoming feed and then by water or air cooling. The cooled effluent enters the middle of the separator vessel and is flashed with a hydrogen rich gas stream leaving the top and a liquid phase leaving the bottom of the separator. This liquid stream is routed to a reboiled stripper column where a debutanized isomerate liquid leaves as the bottom product. The butanes and lighter components that leave the top of the tower are partially condensed to provide reflux to the tower and a liquid product rich in butanes and propane. The uncondensed overhead leaves the stripper condenser drum to be routed to fuel gas or other processes. Details of the isomerization process

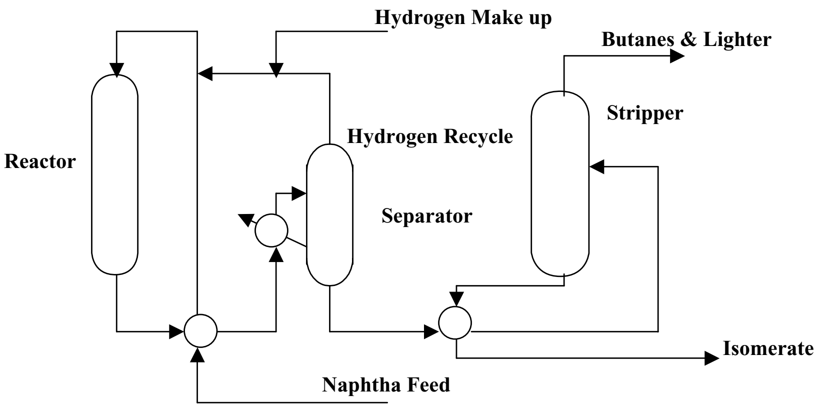


Figure 19.I.1. A process diagram of a typical isomerization unit.

together with a description of the catalyst and chemistry are given in Chapter 9 of this Handbook.

J

Jet fuels

Product specifications are a mechanism by which producers and users of a product identify and control the properties necessary for satisfactory and reliable performance.

Civilian jet fuel

Two organizations have taken the lead role in setting and maintaining specifications for civilian aviation turbine fuel (*jet fuel*): the American Society for Testing and Materials (ASTM) and the United Kingdom Ministry of Defence (MOD). The specifications issued by these two organizations are very similar but not identical. Many other countries issue their own national specifications for jet fuel; these are very nearly or completely identical to either the ASTM or MOD specifications. In the Commonwealth of Independent States (CIS) and parts of Eastern Europe, jet fuel is covered by GOST specifications.

ASTM D 1655 The *Standard Specification for Aviation Turbine Fuels* includes specifications for three commercial jet fuels: two kerosene-type fuels (Jet A and Jet A-1) and a wide-cut fuel (Jet B). Jet A is used for almost all domestic commercial aviation flights in the United States.

Defense Standard 91-91 The United Kingdom Ministry of Defense maintains this specification (formerly titled DERD 2494) for Jet A-1, which is used for most civil aviation fuels outside the United States and the CIS. There are minor differences between the DEF STAN 91-91 Jet A-1 and ASTM D 1655 Jet A-1 specifications.

CGSB-3.22 This Canadian General Standards Board specification covers wide-cut fuel (Jet B) used in parts of Canada and Alaska.

GOST 10227 This Russian specification covers the light kerosene-type fuel, TS-1, used in the CIS and parts of Eastern Europe, along with T-1, T-2, and RT grades of fuel.

Joint Checklist A group of oil companies that operate aviation fuel systems internationally have combined the most restrictive requirements from ASTM D 1655 and DEF STAN 91-91 into a single document: *Aviation Fuel Quality Requirements*

Table 19.J.1. Comparison of civil jet fuels

Specification	ASTM D 1655	Def Std 91–91
Aromatics Vol% Max	25	25
Distillation °C		
10% recovered Max	205	205
50% recovered Max	report	Report
90% recovered Max	report	Report
End point	300	300
Flash point °C Min	38	38
Density @ 15°C kg /M3	775–840	775–840
Freezing point °C Max	−40	−47

for Jointly Operated Systems. This publication is sometimes referred to as the *Joint Checklist*.

International Air Transport Association IATA publishes a document entitled *Guidance Material for Aviation Turbine Fuels Specifications*. The guidance material contains specifications for four aviation turbine fuels: three kerosene-type fuels (Jet A, Jet A-1, and TS-1) and one wide-cut fuel (Jet B). Jet A meets the ASTM requirements, Jet A-1 meets the Joint Checklist requirements, TS-1 meets the Russian GOST requirements, and Jet B meets the Canadian CGSB requirements.

Military jet fuel

The governments of the United States and many other countries maintain separate specifications for jet fuel for military use. The reasons for separate specifications include the operational and logistical differences between the military and civilian systems and the additional demands that high-performance jet fighter engines place on the fuel. Presently two fuels are in widespread use by the U.S. military: JP-5 by the Navy, and JP-8 by the Air Force. Both are kerosene-type fuels. The major difference between them is the flash point temperature, although there are also minor differences in other fuel properties. The minimum flash point temperature for JP-8 is 38°C, and for JP-5 is 60°C. The higher flash point for JP-5 affords an additional degree of safety in handling fuel on aircraft carriers.

The major difference between U.S. military fuels and commercial fuels is in the use of *additives*. Otherwise, JP-8 and Jet A-1 are very similar fuels. Table 19.J.1 provides a comparison between the civilian and military jet fuel specification.

Jetties

Tankers and barges are loaded and unloaded at jetties or docks. In almost all circumstances these facilities for handling petroleum products are separate from those used

for general cargo. Very often tankers, particularly modern ‘Super’ tankers are loaded and unloaded by submarine pipelines at deep water anchorage. Only the ‘Onshore’ jetty facility is described here. Tanker sizes range from small coastal vessels of 10,000 bbl capacity to super tankers in excess of 250,000 bbl capacity. The more common tanker size is one of 140,000 bbl capacity and this size tanker is labeled a T2. This tanker is usually used for product carrying. It can carry as much as three different product parcels at the same time. The larger tankers are usually used for crude oil transportation.

Ideally the jetty size should be sufficient to cater for both these size tankers, and usually at least one of each size at the same time. In some refineries which have jetty facilities these usually include barge loading items also. The barge loading may however be located on remote docking facilities from the larger sea going tankers. A good onshore jetty approach road is mandatory for the operation of the jetty. This is required for safety reasons and the easy approach way for emergency vehicles (such as fire engines and ambulances). The approach road is also required foe the transportation of the operating staff, ship’s crew and the ships chandler vehicles. Usually this approach road is dedicated for jetty use and will be quite independent of any adjacent refinery road.

Finally the location of the jetty must allow sufficient waterway room for tankers to be berthed properly. Tankers arriving from the open sea must have room so that tugs can handle and turn the ship around to face open sea before tying up at the jetty.

A layout plan of a typical tanker jetty is shown in Chapter 13 Figure 13.16. This chapter also includes a description of ideal jetty configuration, and location relative to the refinery site. The item also covers the environmental issue when loading and unloading hydrocarbons.

K

Kerosene

Most straight run kerosenes are desulfurized and routed directly to the finished product blending pools. The exception is in the case of the aviation turbine gasoline (ATG) which will require the kerosene precursor to be treated for aromatics reduction or removal to meet the strict smoke point specifications associated with this finished product. In present day refineries this is accomplished by hydrotreating the kerosene using a nickel catalyst. In older refineries the aromatics contained in the cut were removed as an extract in a process using SO_2 as a solvent. Some details

Table 19.K.1. Specification of some kerosene finished products

Parameters	Reg Kero	ATG	TVO	
Flash point °F	100	<66	100	D-56
Aromatics vol%	–	20	–	D-1319
Temperature @ 20% Max		293°	–	D-86
Temperature @ 50% Max		374°	–	D-86
Temperature @ 90% Max		473°	540	D-86
Final boiling point	572°F	572°	–	D-86
Sulfur Max wt%	0.04	0.04	0.3	D-1266
Smoke point Min	–	25 mm	25 mm	D-1322
Freeze point °C	–	−47	–	D-2386

of the de-aromatization hydro-treating process are given in Chapter 8 of this book. Table 19.K.1 gives the general spec of the kerosene products.

Kinematic viscosity

The Darcey–Weisbach and Colebrook relationships are based on using a Reynolds number which varies inversely with the *kinematic* viscosity. This kinematic viscosity is defined as the Dynamic (or Absolute) viscosity divided by its density, where dynamic or absolute viscosity is force × (time/length squared) and the unit for this is the Poise. The unit most frequently used for the kinematic viscosity is the metric unit—the Stoke. Both viscosities are however usually quoted in the hundredth unit. Thus, absolute viscosity would be the centipoise while the kinematic viscosity would be centistokes.

L

Leaded gasolines

Until the restrictions on lead compounds imposed by the ‘Clean Air’ acts of the 1960s, tetra ethyl lead was used extensively as a gasoline additive to improve Octane Number.

Tetra ethyl lead is a liquid with a gravity of 1.66 and a formula $Pb(C_2H_5)_4$. It is extremely toxic. The restriction of ‘No Lead’ in gasolines promoted further development of the catalytic reformer process to obtain higher conversion. It also influenced the use of the alkylation process and the development of isomerization and the oxygenated compounds as octane enhancers in gasoline. Coupled with this, motor manufacturers

improved their respective auto engine design to operate efficiently on lower octane number fuel. Tetra Ethyl Lead has all but disappeared from the petroleum industry. Details of modern gasoline development are given in Chapter 2 and details of the Octane enhancer processes are given in Chapter 9.

Light end units

The light end units in the refinery produces the light and heavy naphtha cuts, the butane LPG, and the propane LPG products respectively. The straight run light end units take as feed the atmospheric overhead distillate, the overhead distillate from the catalytic reformer stabilizer, and the overhead distillate from a thermal cracker fractionator (if there is one in the configuration). A typical process flow schematic showing the sequence of the light ends unit is given as Figure 19.L.1.

The long range naphtha as the distillate from the atmospheric crude distillation overhead condensate drum is preheated, usually by heat exchange with the debutanizer bottom product before entering the debutanizer tower. Here the butanes and lighter

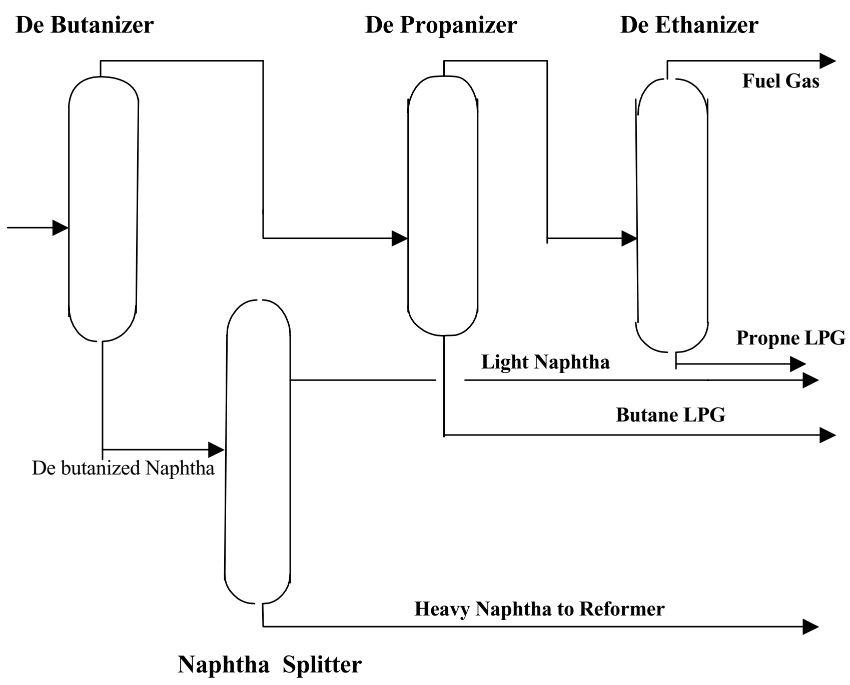


Figure 19.L.1. Process flow schematic for light ends plant.

fractions are removed as the overhead distillate. The bottom product from this tower is the long-range debutanized naphtha. This cut enters the naphtha splitter tower where it is fractionated to meet the specification of light naphtha as the overhead distillate product and heavy naphtha as the bottom product. The light naphtha fraction is routed to the gasoline pool for blending, while the bottom product is the feed to a catalytic reformer.

The overhead distillate from the debutanizer is preheated and enters the de-propanizer tower. Butane LPG is the bottom product from this tower and after treating to remove any sulfur products is routed to the LPG pool. The overhead distillate from the de-propanizer contains propane and lighter components. This is preheated and enters the de-ethanizer column. There is no overhead distillate product from this tower. The overhead product is simply the components lighter than propane and leaves as a gas to the refinery's fuel gas system. Some of the overhead vapor leaving the tower top is partialy condensed to produce the tower reflux. The bottom product from this tower is propane LPG and is routed to the LPG pool.

All three towers are reboiled and are operated with overhead reflux. Full details of this process is given in Chapter 4. A similar process is utilized for the light ends from the FCCU. This is usually kept separate from the straight run process described above. Wild distillates (i.e., containing the light ends) from the catalytic reformer stabilizer and the thermal cracker are routed to the straight run light end units.

Linear programming

This is a computerized technique that came into prominence during the late 1960s and early 1970s. It is used extensively now by most refiners to:

- Optimize new process configurations
- Plan the refinery operation
- Select crude oil feed slate and product slate

The technique uses equations (linear) that represent the properties of the crude feed and the resulting products. These equations also describe the blending characteristics of the components making up the finished product slate. Included also are the cost parameters such as the price of crude feed, the refinery fence selling price of products, operating cost, and any other relevant cost centers (such as licensing fees, interest on loans, etc.). These equations form a mathematical model and a suitable programmed computer is used to solve these equations to meet the objective function subject to the constraints of the analysis. Some further details describing linear programs is given in Appendix E.

LPG—liquefied petroleum gas

Refineries produce two types of LPG (liquefied petroleum gas) products, butane LPG and propane LPG. These two products are recovered in the straight run light ends units as described above. They are routed to finished product storage after treating for the removal of sulfur in the form of mercaptans. Their specifications are as follows:

Propane LPG

Vapor pressure psig	255 max
C_1 hydrocarbons mole%	0.1 max
C_2 hydrocarbons mole%	5.0 max
C_3 hydrocarbons mole%	95 min
C_4 hydrocarbons & heavier mole%	4.0 max (expressed as C_5)
Total unsaturated hydrocarbons mole%	1.0 max
Total sulfur content wt%	0.01 max
Mercaptans grains/100 cuft at STP	3.0 max
H_2S content	Nil.

The product shall not contain harmful quantities of toxic or nauseating substances and shall be free of entrained water

Butane LPG

Vapor pressure psig	70–85
C_1 hydrocarbons mole%	Nil
C_2 hydrocarbons mole%	0.5 max
C_5 hydrocarbons mole%	2.0 max
Total sulfur Wt%	0.01 max
Mercaptan grains/100 cuft at STP	2.0 max
H_2S content	Nil

The LPG's are utilized widely in industry and domestically as portable fuel source. The fact that they are liquids under pressure and are stored in moveable cylinder containers gives them prominence in the work place, at home, and in outside recreation areas. Propane LPG is used domestically for outdoor barbecues, in recreational vehicles, for cooking and heating, and on private boats, etc. Butane LPG is used mostly in industry as a portable heat source. LPGs are also used as automotive fuels. In the U.S. propane is often used in agricultural tractors. Butane LPG is often used in Europe for taxi fleets, etc.

Lube oils

Some, not all, refineries produce lubricating oils. These are considered non-energy products but are essential to modern living just as much as the energy products of

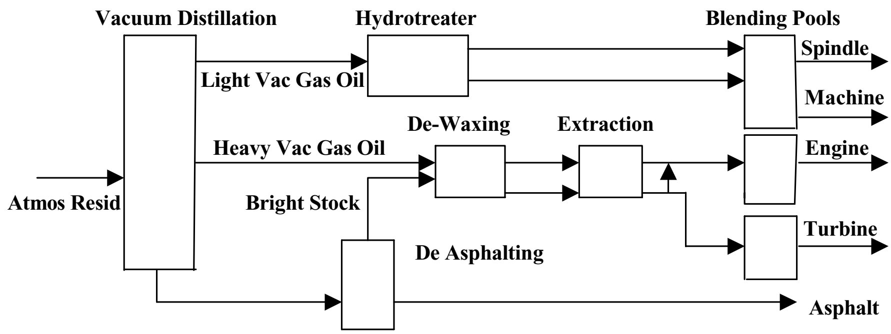


Figure 19.L.2. A schematic of a lube oil processing configuration.

petroleum. About 3–10 grades of basic lube oil components are produced and can be blended to meet the many grades of light lube oils, engine lubes and heavy turbine lube oils. The production of these basic lube products commences with the vacuum distillation of atmospheric residue. The processes to arrive at the blendable basic stocks follow the block flow diagram shown as Figure 19.L.2.

The atmospheric residue feed is vacuum distilled to provide two distillate side streams and a heavy bituminous residue. The light distillate side stream is hydro-treated to saturate any olefins present and, thus, improve the product color. It is then split in a vacuum distillation tower to produce the very light spindle oil lube and the slightly heavier machine oil lube. The bottom side stream distillate from the vacuum unit is routed to a de-waxing plant and then to a solvent extraction plant for color improvement. Both these units may be operating in a blocked operation with a raffinate from propane de-asphalting unit. This unit processes the vacuum residue to remove the asphalt leaving the de-asphalted oil, called 'bright stock' to be dewaxed and olefin extracted in the blocked operation through these two plants. The treated 'bright stock' is the base stock for the heavy turbine lube oils. Details of the lube oil production processes are given in Chapter 12.

M

Mass spectrometry

Mass spectrometry is concerned with the separation of matter according to atomic and molecular mass. It is most often used in the analysis of organic compounds of molecular mass up to as high as 200,000 Daltons, and until recent years was largely

restricted to relatively volatile compounds. Continuous development and improvement of instrumentation and techniques have made mass spectrometry the most versatile, sensitive and widely used analytical method available today. One of its major uses in the petroleum refining industry is for the production of distillation curves such as TBP and EFV. This technique does away with the cumbersome distillation apparatus previously used for this purpose. It is also by far the more accurate method.

Material balances

Material balances form the basis for plant design, and are essential in refinery operation to account for gains and/or losses in the refinery's daily production. They are also essential in process plant audits and trouble shooting. The primary material balance in the design of a refinery is that for the atmospheric and vacuum crude distillation unit. For this balance the TBP distillation curve (usually from the crude assay) is split into real components up to C_5's or C_6's and then into mid boiling point or mid volume point pseudo components. The splitting of the crude in this way provides the component breakdown for the product cuts and the volume, mass, and the number of moles, together for the same information for the whole crude feed. Details on the development of the material balances are given in Chapter 3–12. The material balance in all cases is complete and correct when the quantities into the process equals the total quantities out when expressed in mass (weight) units. Volumes and mols in and out may differ because of chemical reactions and/or thermal and pressure effects.

Mechanical flow diagrams

This type of flow diagram is sometimes referred to the P&ID or very often the Engineering Drawing. Details of this type of drawing is given under the item flow sheets.

Metals in crude oil

Metallic organic compounds have a deleterious effect on some products, and are also usually poisonous to catalysts in some processes. The most common metals met with are:

- Sodium
- Nickel
- Vanadium

and sometimes mercury, etc. in the associated gas streams.

Most of these metallic compounds are found in the asphalt portion of the crude oil and are usually deeply imbedded in the asphaltene molecules. In the production of fuel oil the metal content of the fuel makes the product problematic to the steel production companies who use fuel oil in their processes. Secondly, in the upgrading of the 'bottom of the barrel' using a catalytic process (such as hydrocracking or fluid catalytic cracking) these metallic compounds deteriorate the catalyst life and performance of the processes. Much has been done in the last decade to improve the catalysts to withstand metals. However, in many cases the true solution to the presence of metals in the crude is to de-asphalt the heavy vacuum residue and route the de-asphalted oil as the cracker feed. Not all crude oils contain metal impurities in quantities that cause process problems. The deasphalting process (as propane deasphalting unit) is described in Chapter 11.

Mid boiling point and mid volume point components

These have been defined and described earlier in this Part 2, 'Component balances', and also in Chapter 1.

N

Naphtha

There are usually two straight run naphtha cuts produced from crude. These are:

- Light naphtha (sometimes called light gasoline)
- Heavy naphtha

Both these naphtha cuts form part of the atmospheric crude distillation overhead distillate product. This product also contains all of the light ends of the crude oil feed. The stream is therefore debutanized with the components butane and lighter being routed to the light ends unit for further fractionation.

The naphtha stream that leaves the bottom of the debutanizer is fed to a naphtha splitter where it is fractionated to produce the two naphtha cuts. The light naphtha as the splitter's overhead distillate product contains most of the crude's C_5's and much of the paraffin portion of the crude's C_6's. Heavy naphtha is recovered as the splitter's bottom product. This product will contain the heavier naphthenes and will be a suitable feed for a catalytic reformer. The light naphtha has a TBP distillation range of C_5 to around 190°F and is often used as feed to steams crackers for the production of

light olefins. The heavy naphtha as the feed to the catalytic reformer consists of a cut of about 190°–360°F. This end point of 360°F can vary depending on the severity operation of the catalytic reformer, the volatility specification of the finished gasoline, and the refinery's production requirements.

The non energy product refineries

There are two major types of non-energy refineries. They are:

- The lube oil refinery
- The petrochemical refinery

These two production units are usually part of a conventional energy refinery, which makes it convenient for obtaining their respective feedstocks and for using common facilities such as loading stations and jetty. The lube oil refinery has been described in an earlier item. More information on this subject is found in Chapter 12. This chapter also details the production and properties of the asphalt product of this type of refining.

The petrochemical refinery

This refinery is concerned with processing products generated by the energy portion of the refining of crude oil into suitable feed streams to the:

- Production of aromatics
- Production of olefinic products

Both of these types of petrochemical refineries have been described briefly in Chapter 1. Only the production of aromatics is dealt with in detail.

The aromatics referred to here will be the more common with respect to crude oil refining. These are:

- Benzene
- Toluene
- Ethyl benzene
- Para-xylene
- Meta-xylene
- Ortho-xylene

The configuration described here begins with a mixed aromatic stream which has been obtained by catalytic reforming of a high naphthene content naphtha (usually from a hydro-cracking process). The reformate from this high naphthene feed is very rich in

the aromatics listed above. To increase the aromatic content as feed to the aromatic complex the aromatics are separated from the remaining paraffins by an extraction process. The rich aromatic feed is separated into the required products by a series of distillations, a crystallization or adsorption process, an aromatic isomerization process, and α dealkylation process. The block flow diagram is shown as Figure 12.18 of Chapter 12.

In this particular configuration the purpose is to maximize benzene, toluene, and ortho xylene at the expense of ethyl benzene, meta and para-xylenes. To recover para-xylene all that would be required is an adsorption or crystallization unit before the isomerization unit.

O

Octane number

Octane numbers are a measure of a gasoline's resistance to knock or detonation in a cylinder of a gasoline engine. The higher this resistance is the higher will be the efficiency of the fuel to produce work. A relationship exists between the antiknock characteristic of the gasoline (Octane Number) and the compression ratio of the engine in which it is to be used. The higher the octane rating of the fuel then the higher the compression ratio of engine in which it can be used. By definition, an octane number is that percentage of iso-octane in a blend of iso-octane and normal heptane that exactly matches the knock behavior of the gasoline. Thus, a 90 octane gasoline matches the knock characteristic of a blend containing 90% iso-octane and 10% n-heptane.

The knock characteristics are determined in the laboratory using a standard single cylinder test engine equipped with a super sensitive knock meter. The reference fuel (iso octane and C7 blend) is run and compared with a second run using the gasoline sample. Two octane numbers are used: the first is the research octane number (RON) and the second is the motor octane number (MON). The same basic equipment is used for both octane numbers, but the engine speed is increased for the motor octane number. The actual octane number obtained in a commercial engine would be somewhere between the two numbers. The significance of the two octane numbers is to evaluate the sensitivity of the gasoline to the severity of the operating conditions in the engine. Invariably the research octane number is higher than the motor octane number, the difference between them is quoted as the 'sensitivity' of the gasoline.

The pump octane posted in the U.S. is (RON + MON)/2. In Europe often only RON is given.

Offsite systems

Among the major units found in most refinery offsite systems are:

- Storage
- Product blending
- Road and rail loading
- Jetty facilities
- Waste disposal
- Effluent water treating

Storage facilities

Crude oil feed and processed products are stored in storage tanks of various sizes and types. These tanks are usually located together in the refinery area suitably defined as 'the Tank Farm'. Most refinery storage tanks fall into the following categories:

- Atmospheric storage
- Pressure storage
- Heated storage

Details of all these type of tankage are given in Chapter 13.

Atmospheric storage
As the name implies, all atmospheric storage tanks are open to the atmosphere, or are maintained at atmospheric pressure by a controlled vapor blanket. These tanks fall into two categories:

- Cone roof tanks
- Floating roof tanks

Cone roofed tanks. Used for the storage of non-toxic liquids with fairly low volatility. In its simplest form the roof of the tank will contain a vent, open to atmosphere, which allows the tank to "breathe" when emptying and filling. A hatch in the roof also provides access for sampling the tank contents. In oil refining this type of tank is used for the storage of gas oils, diesel, light heating oil, and the very light lube oils (e.g., spindle oil).

Floating roofed tanks. Light volatile liquids may also be stored at essentially atmospheric pressure by the use of "Floating Roof" tanks. The roof of this type of storage tank literally floats on the surface of the liquid contents of the tank. In this way the air space above the liquid is reduced to almost zero, thereby minimizing the amount of liquid vaporization that can occur. The roof is specially designed for this service

and contains a top skin and a bottom skin of steel plate, held together by steel struts. These struts also provide strength and rigidity to the roof structure. The roof moves up and down the inside of the tank wall as the liquid level rises when filling and falls when emptying. Liquids stored in this type of tank have relatively high volatilities and vapor pressures such as gasoline, kerosene, jet fuel, and the like. In oil refining the break between the use of cone roof tank and floating roof is based on the "flash point" of the material. Normally this break point is for materials with a flash point of 120°F or below. Floating roof tanks (very large in capacity) are used for storing the crude oil feed. Diagrams of a cone roof tank and a floating roof tank are shown (Figure 19.O.1) as Figures 13.5 and 13.6 in Chapter 13.

Pressure storage
Pressure storage tanks are used to prevent or at least minimize the loss of the tank contents due to vaporization. These types of storage tanks can range in operating pressures from a few inches of water gauge to 250 psig. There are three major types of pressure storage. These are:

- Low-pressure tanks—These are dome roofed tanks and operate at a pressures of between 3 ins water gauge and 2.5 psig.
- Medium-pressure tanks—These are hemispheroids that operate at pressures between 2.5 psig and 5.0 psig, and spheriodal tanks that operate at pressures up to 15 psig.
- High-pressure tanks—These are either horizontal "bullets" with ellipsoidal or hemispherical heads or spherical tanks (spheres). The working pressures for these types of tanks range from 30 to 250 psig. The maximum allowable is limited by tank size and code requirements. For a 1,000 bbl sphere, the maximum pressure is 215 psig, for a 30,000 bbl it is 50 psig. These pressure limits can be increased if the tank is stress relieved.

Although it is possible to store material in tanks with pressures in excess of 250 psig, normally when such storage is required refrigerated storage is usually a better alternate.

Heated storage tanks
Heated storage tanks are more common in the petroleum industry than most others. They are used to store material whose flowing properties are such as to restrict flow at normal ambient temperatures. In the petroleum industry products heavier than diesel oil, such as heavy gas oils, lube oil, and fuel oil are stored in heated tanks. Most often tanks are heated by immersed heating coils or bayonet type immersed heaters. Steam is normally used as the heating medium. Where immersed heating is used the tank is agitated usually by side located propeller agitators. External circulating heating is used for tanks if the contents are mixed by means of jet mixing. External tank heating is used when there is a possibility of a hazardous situation occurring if an immersed

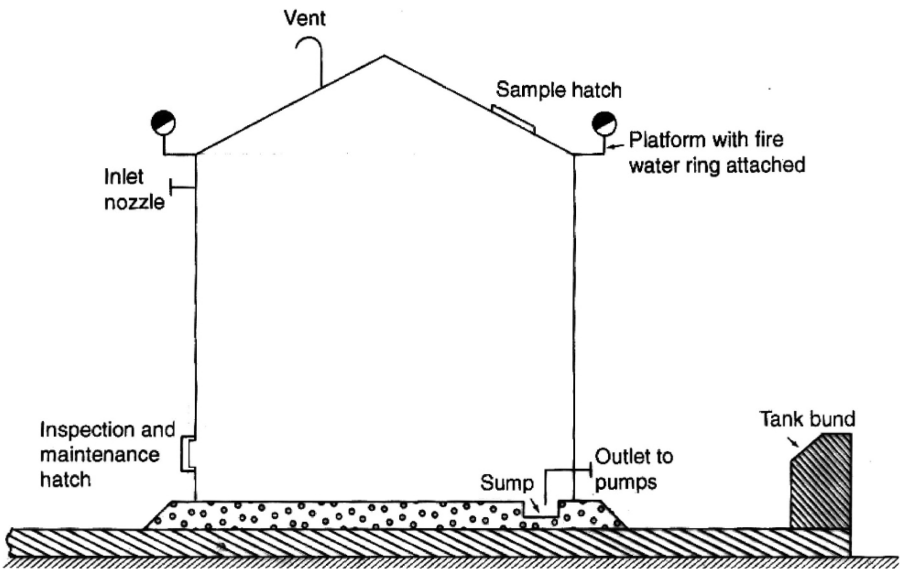


Figure 13.5.

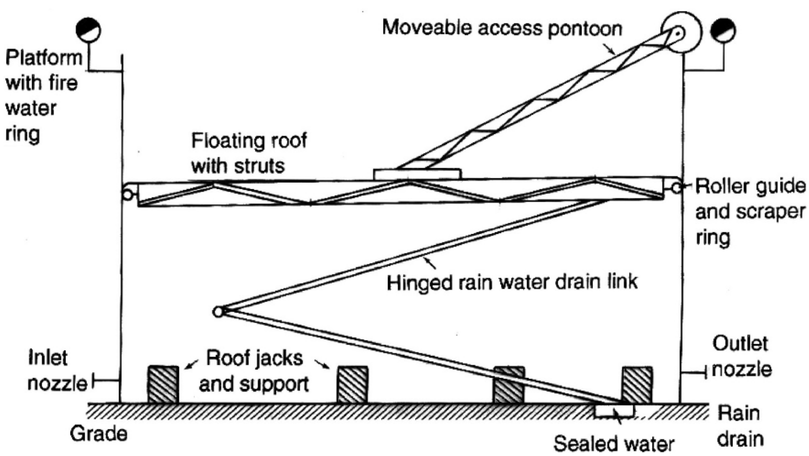


Figure 13.6.

Figure 19.O.1. Diagram of a cone roof tank and a flooting roof tank.

heater leaks. A calculation procedure for tank heater sizing is included in Chapter 13.

Product blending facilities

Blending is the combining of two or more components to produce a desired end product. The term in refinery practice usually refers to process streams being combined to make a saleable product leaving the refinery. Generally these include gasolines and middle distillates such as jet fuel, kerosene, diesel, and heating oil. Other blended finished products will include various grades of fuel oil and lube oil. The blending of the process streams is accomplished either by batch blending in blending tanks or in-line blending in the pipe line itself.

In-line versus batch blending
In batch blending the components are routed separately into a single receiver tank where they are mixed and tested to ensure the mixed product meets the finished product specification. In the case of in-line blending the component streams are routed through automatically operated flow valves to a finished product tank. With modern computerized control technology in-line blending is becoming the more common form of blending process.

The in-line blender operation
An in-line blender is essentially a multiple stream controller with feed-back. The controller itself is a computer into which the recipe for the blend is programmed. The controller automatically starts the pumps for the blend components and motivates the flow control valves on the component lines. These control valves are reset by computer inert-action to meet the required component quantities for finished product specification. A series of on line analyzers located in the blend run down lines, monitor the finished product properties and, in turn, reset the control valves.

Road and rail loading facilities

The extent of product shipping facilities required in a chemical or petroleum complex depends on the size of the complex, the local market, the number of different products to be shipped and the market to be supplied. Normally the shipping facilities installed in most plants are sufficient to cater for normal product handling and the flexibility required for seasonal demands. The capacity of these facilities will almost invariably exceed the plant's total production.

The most common method of shipping product is by road or rail in suitably designed tanker cars. In the case of large complexes located on coastal or river side sites

shipping by barge or ships is feasible to carry the bulk of the plant products. Chapter 13 describes the loading of road and rail cars under the following subject headings:

- Loading rates
- Loading equipment
- Loading arrangements

Loading rates are described with details on the calculation procedures to arrive at these rates example calculations are provided. Drawings of loading equipment and their typical arrangements are also provided in this section of Chapter 13.

Jetty and dock facilities

Tankers and barges are loaded and unloaded at jetties or docks. In almost all circumstances these facilities for handling petroleum products are separate from those used for general cargo. Very often tankers, particularly the modern 'Super' tanker are loaded and unloaded by submarine pipelines at deep water anchorage. This section of Chapter 13 deals only with onshore docking facilities. The following items in this section of the chapter are:

- Jetty size and location
- Equipment
- Loading rates
- Ballast handling
- Slop and spill collection facilities

Jetty size and location covers the need to accommodate the various tanker or barge sizes. It continues with the parameters to be considered in the location of the jetty itself. This topic includes consideration of the access to the jetty and the depth of the water at the location. The jetty must be close to the refinery's tank farm and must cater for sufficient pipe-way. Just as important too is that the jetty has good approach road and parking facilities. These topics are discussed in some detail.

The equipment used for tanker loading and unloading is described in detail with supporting diagrams.

In the item on loading (and unloading) rates emphasis is placed on the relatively high pumping rates experienced for this function. The item covers the rates usually used for normal tanker size and those for the barge loading facilities. The other items cover the disposal of the ships' ballast and the collection of the spills and leaks that occur in the loading/unloading activities. The collection of these spills is achieved by temporary booms placed around the vessels. Other topics include communication with shore facilities and the mooring facilities. These topics are supported by diagrams where applicable.

Waste disposal and water effluent treatment

All process plants, including oil refineries produce large quantities of toxic and/or flammable material during periods of plant upset or emergencies. Properly designed Flare and Slop handling systems are therefore essential to the plant operation. This section of Chapter 13 describes and discusses typical disposal systems currently in use in the oil refining industry where the hydrocarbon is immiscible with water. Where the chemical is miscible in water special separation systems must be used. The item covering waste disposal systems is shown in a block flow diagram for a typical modern refinery. The system shown consists of three separate collection systems being integrated to a flare and a slops rerun system. A fourth system is included for the disposal of the oily water drainage with a connection to the flare and a separate connection for any oil laden skimming. Further description and discussion of these disposal systems is given in the following sections covering:

- Blow-down and slop disposal
- Flares

The description and discussion of these systems highlights the equipment used and, where applicable, the sizing parameters for some of these items. All the descriptions are further illustrated by diagrams.

This section of the offsite systems deals with the treating of waste water accumulated in a chemical process complex before it leaves the complex. Over the years requirements for safeguarding the environment has demanded close control on the quality of effluents discharged from chemical and oil refining plants. This includes effluents that contain contaminants that can affect the quality of the atmosphere and those that can be injurious to plant and other life in river waters and the surrounding seas. Effluent management in the oil industry has therefore acquired a position of importance and responsibility to meet these environmental control demands. This topic is further explored in Chapter 14, under the title of "Environmental Control and Engineering in Petroleum Refineries". The item in Chapter 13 deals with the broad principals and methodology of treating water effluents from paved area run off, ship ballast water, and effluent from the slop and spillage facilities. The major processing equipment to handle most effluent treating in the petroleum refinery is the API separator. A detailed description and design parameters of this equipment is given in Chapter 14. Other effluent treating processes such as flocculation and coagulation are described in Chapter 13.

Olefins

Although the major families or homologues of hydrocarbons found in all crude oils as described earlier are paraffins, cyclic paraffins and aromatics, there is a fourth group.

These are the unsaturated or olefin hydrocarbon. They are not naturally present in any great quantity in most crude oils, but are often produced in significant quantities during the processing of the crude oil to refined products. This occurs in those processes that subject the oil to high temperature for a relatively long period of time. Under these conditions the saturated hydrocarbon molecules break down permanently losing one or more of the four atoms attached to the quadravalent carbon. The resulting hydrocarbon molecule is unstable and readily combines with itself (forming double bond links) or with similar molecules to form polymers. An example of such an unsaturated compound is as follows:

$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & = & C & - & H \end{array} \qquad \text{Ethylene.}$$

Note the double bond in this compound linking the two carbon atoms.

Overflash

Overflash is a term normally associated with the design of crude atmospheric or vacuum towers. Its objective is to provide additional heat (over and above that set by the product vaporization required) required by the process to generate the internal reflux required by the process. It also influences the flash zone conditions of temperature and partial pressure of the hydrocarbon vapor feed. Usually it is fixed at between 3 and 5 vol% on crude. This atmospheric flash temperature is now adjusted to the temperature at the previously calculated partial pressure existing in the flash zone. A further description and the purpose of overflash is given in Chapter 3.

P

Packed towers

Although the use of trays is generally the first choice for fractionation and absorption tower applications, there are two major instances where packed towers are preferable. These are:

- Small diameter towers (below 3 ft diameter)
- At the other end of the spectrum packing in the form of grids and large stacked packed beds have superceded trays in vacuum distillation towers whose diameter range up to 30 ft in some cases. This is because packing offers a much lower pressure drop than trays

The packing in the tower itself may be stacked in beds on a random basis or in a defined structured basis. For towers up to 10–15 ft the packing is usually dumped or randomly packed. Above this tower size and depending on its application the packing may be installed on a defined stacked or structured manner. For practical reasons and to avoid crushing the packing at the bottom of the bed the packing is installed in beds. As a rule of thumb packed beds should be around 15 ft in height. About 20 ft should be a maximum for most packed sections.

Properties of good packing are as follows:

- Should have high surface area per unit volume
- The shape of the packing should be such as to give a high percentage of area in active contact with the liquid and the gas or in the two liquid phases in the case of extractors
- The packing should have favorable liquid distribution qualities
- Should have low weight but high unit strength
- Should have low pressure drop, but high coefficients of mass transfer

Some data on the various common packings together with a typical packed tower layout are given in Chapter 18. This chapter also gives design procedures and data for packed towers in general. These procedures and characteristics of the packed tower are supported by diagrams and graphical correlations where applicable.

Petrochemical refineries

(See the previous item on 'Non-Energy Product Refineries').

Planning refinery operations

The basic organization of an oil company consists essentially of three main departments:

1.0 The marine department
2.0 The refining department
3.0 The marketing department

The functions of these three main departments are co-ordinated by a supply department. This department undertakes this role in accordance with the following sequence:

1.0 Marketing department informs the supply department with the quantities of products they can sell.
2.0 Supply department, after making adjustments for stock levels, advises the refinery of the quantity of each product required.

3.0 The refining department advises the supply department of the actual quantities they can produce and how much crude they will require to do so.
3.0 The supply department arranges with the marine department for the necessary shipping to:
- Provide the crude
- Lift the products
- Import the quantities that cannot be produced
  Each refinery organization contains a planning department whose function is to put together the Monthly Running Plan. The main uses of the running plan are to provide data for:
- Keeping the supply department and the company executives informed
- Provide information for long term chartering of ships
- Arrangement of import programs
- Pinpoint future product quality and equipment difficulties

The plans reflect inventory surplus or deficit in immediate stocks and those due in the short term and over a period of around 18 months to satisfy the objectives of the supply department. It is also the basis of the refinery's running program in the short term. By that is meant the establishment of the refinery's process plant conditions and product blending programs, storage schedule, etc., on a day by day basis. The program when extended to each quarter of the 18 months' duration, alerts the supply department of possible shortfalls, crude slate requirements, and the refinery's possible processing constraints. These constraints take into consideration scheduled shut downs, storage capabilities and the like. Full details of a refinery plan together with examples of its development are given in Chapter 17.

Plant commissioning

The sequence of events that ends with a plant or plants being fully operational follows the same lines whether it refers to a single unit or a complex of many units such as a refinery.

The commissioning activities fall into the following sequence of events:

- Pre-energizing activities
- Energizing the plant
- Conditioning equipment, calibrating instruments, and setting relief valves
- Final check out, and closing up all vessels
- Preparation for "start up"
- Start up
- Lining out
- Performance test runs and guarantee test run

Pre-energizing activities

These are the activities when the contractor or the refinery's own staff hands the plant over to the commissioning operators. At this stage the plant is not connected to power, steam, water, drains, etc and contains no hazardous material. The commissioning team's objective now is to check the hardware against specifications and the engineering drawings. This activity has been given the title 'Punch Listing'. Although the contractor has flushed the plant out before handover a further and more thorough flushout is usually done at this "safe plant" stage when utility lines and underground lines can also be flushed out.

Energizing the plant

When 'punch listing' is complete to everyone's satisfaction the plant can be energized. This includes the connection to power and the other utilities. The commissioning of the fuel systems indicates that the plant is now a 'Hazardous Area' and all regulations pertaining to this type of area come into effect.

Conditioning equipment

Reactors, certain pipelines carrying corrosive material, and other items such as the flare, and heater boxes which are refractory lined require some conditioning before being put into use. These conditioning procedures are usually detailed by the manufacturers. As most of these procedures call for an energized plant they are carried out by the commissioning team.

Final check out, and closing up of all vessels

This will be the last opportunity to check such items as the internals of towers, fractionation trays, condition of refractory and other linings, hold up grids, distributors, and the bottom of the tower baffling system (to and from the reboiler). A final check-out of the piping layout also needs to be carried out at this point. When satisfied that all is satisfactory the commissioning supervisor will authorize the following final pre-startup activities to be completed:

- Catalyst loading (where applicable)
- Loading the tower packing where applicable
- Closing up all vessels using the permanent gaskets

In cases where equipment has been subject to a caustic wash the temporary silica level gauges used during the wash are replaced by the specified operational ones.

With the completion of these final checks and vessel close up, the plant is now ready for start up.

Start up and lining out

The activities and their sequence for starting up the plant are carried out as described in the operating manual. In the case of an oil refining plant for example the first activity is to eliminate air from the plant systems. This is done by using water or steam or inert gas or a combination of all three.

After the purging comes the introduction of the cold feeds. In the case of units that contain reactors and use hydrogen under pressure a leak testing program is required. Where water has been used for purging, the water is replaced by the oil feed. This is termed the 'oil squeeze'. Start up may be defined as beginning when the purge program shows conditions to be safe to apply heat into the plant.

Pour points

The 'Pour Point' of an oil is the temperature at which the oil ceases to flow. It is usually a test applied to middle distillates, lube oils, and fuel oils. The test itself is quite simple and requires the sample oil to be carefully treated before the test and to reduce its temperature in a controlled and orderly way. Unlike most other petroleum properties pour points of two or more components cannot be blended directly to give a pour point of the blended stock. Blending indices are used with the volumetric composition of the blend components for this purpose. Details of the blending for 'Pour Point' are given in Chapter 1 while details of the test itself are given in Chapter 16.

Predicting product properties

Product properties are predicted from a composition of real components and of pseudo components that make up the product streams. Most crude oil assays will include the composition of the light ends in terms of volume or weight percent on crude. The light ends usually include C1 to C5's inclusive. The remainder of the crude oil may be divided into pseudo components based on the TBP curve. Details of this are given in Chapter 1 and further illustrated in Sections of Chapter 2 and Chapter 3.

The pseudo components are either expressed as wt% or vol% on whole crude, and are identified as either mid boiling point or mid volume on crude. This concept is further

defined again in Chapter 1, Chapter 2, and Chapter 3 and under the title of Mid Boiling Points in this chapter. From the assay data and curves, properties such as specific gravity, sulfur content, pour points, etc. are given to these pseudo components either in terms of boiling point or their mid volume point on crude. In most cases the property of a cut is determined by the sum of these component properties times their vol% or wt% in the cut. In a few cases however the direct multiple of properties and percentages is not acceptable to define the overall property of the cut. The most notable are flash points of blended cuts, and pour points. Here blending indices are used as the multiple of volume composition. These indices are given in Chapter 1. The sulfur content of a product is always quoted as a percent by weight of the product. In this case therefore both the pseudo components and the sulfur content (from assay) are converted to weight.

The flash point of a product is related to its ASTM distillation by the expression:

$$\text{Flash Point} = 0.77\,(\text{ASTM 5\% in }^\circ\text{F}–150^\circ\text{F})$$

To determine the viscosity of a blend of two or more components, a blending index must be used. A graph of these indices is given in Maxwell's "Data Book on Hydrocarbons", and part of this graph is reproduced as Figure 1.08 in Chapter 1. Using the blending indices and having divided the TBP curve into components as before, the viscosity of the fraction can be predicted as shown in the following example:

Component	Vol%	Mid BPt °F	Viscosity Cs 100°F	Blending index	Viscosity factor
	(A)			(B)	(A × B)
1	13.0	410	1.49	63.5	825.5
2	16.5	460	2.0	58.0	957
3	21.0	489	2.4	55.0	1,155
4	18.0	520	2.9	52.5	945
5	18.5	550	3.7	49.0	906.5
6	13.0	592	4.8	46.0	598
Total	100.0				5,387.0

$$\text{Overall Viscosity index} = \frac{5{,}387}{100} = 53.87$$

From Figure 1.08 (in Chapter 1) an index of 53.87 = 2.65 Cs.
(Actual plant test data was 2.7 Cs).

The prediction of molecular weights of product streams are more often required for the design of the processes which are going to produce those products. There are other more rigorous calculations that can and are used for definitive design and in

building up computer simulation packages. The method presented here is a simple method by which the mole weight of a product stream can be determined from a laboratory ASTM distillation test. The result is sufficiently accurate for use in refinery configuration studies and the like. A relationship exists between the mean average boiling point of a product (commonly designated as MEABP), the API gravity, and the molecular weight of petroleum fractions. This is described in detail in Chapter 1.

Preheat exchanger train

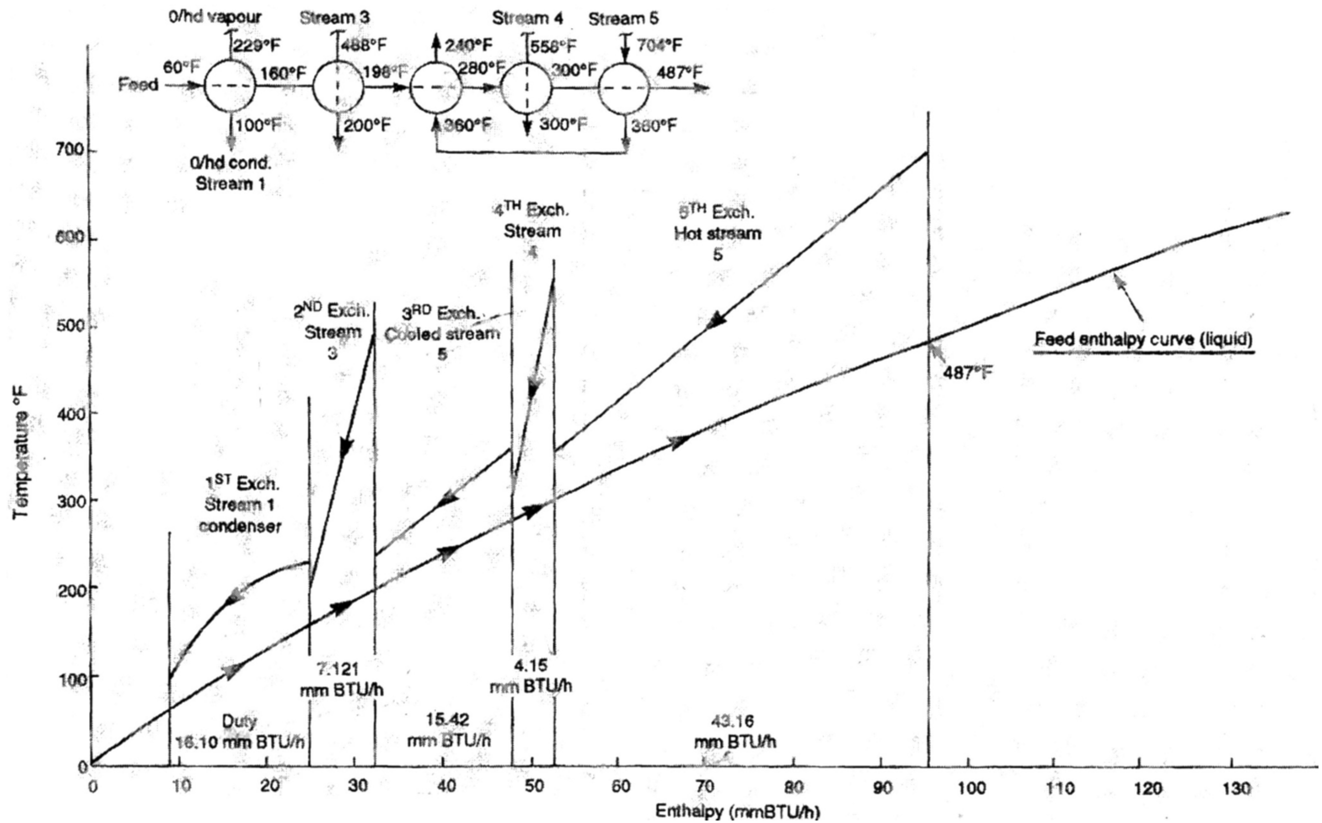
In most distillation processes heat recovery by heat exchange is of great importance. In the design of major processes such as the crude oil distillation unit, cracker recovery units and the like the optimization of this heat recovery concept is of paramount importance. The method best adopted to undertake this heat recovery concept is described in detail in Chapter 3. Briefly the method consists of examining several configurations of a heat transfer train, applying "pinch" analysis a cost data to the equipment, and to determine the terminal feed temperature of each configuration. This end temperature relates to the heater duty required and therefore to the fuel required by the heater. An economic balance may then be made to select the optimum heat exchanger configuration. Developing the various configurations is made by using the total enthalpy of the feed (in this case the crude oil feed to the atmospheric distillation unit) and the total enthalpies of the exchanged streams. This is shown by Figure 3.14 of Chapter 3, and is reproduced on page 1250.

Process guarantees

Among the items of major concern to the operating refinery staff and the engineering contractor in the design, procurement, and construction of a grass roots process or indeed a revamped process, is the final process guarantees that are developed and accepted. The process guarantees may begin to be developed as soon as a firm process has been established and manufacturers' guarantees obtained for the performance of the various manufactured items of equipment.

The process performance is tied also to a guarantee of its efficiency. This will be in terms of a guarantee of the utility consumption in the plant whilst operating on the design throughput and conditions. These guarantees as written will differ from process to process but will usually follow a pattern or format.

- Description of the feed in terms of throughput, composition, or source (in the case of crude oil)



0/hd vapour
229°F
Feed
60°F
160°F
100°F
0/hd cond.
Stream 1
Stream 3
488°F
198°F
200°F
240°F
280°F
360°F
Stream 4
556°F
300°F
300°F
Stream 5
704°F
487°F
360°F
1ST Exch.
Stream 1
condenser
2ND Exch.
Stream
3
3RD Exch.
Cooled stream
5
4TH Exch.
Stream
4
5TH Exch.
Hot stream
5
Feed enthalpy curve (liquid)
487°F
Duty
16.10 mm BTU/h
7.121
mm BTU/h
15.42
mm BTU/h
4.15
mm BTU/h
43.16
mm BTU/h
Temperature °F
Enthalpy (mmBTU/h)

Figure 3.14.

- Design operating conditions and the guarantee of the product specification at these conditions
- A guarantee of the hydraulic capacity of the process system
- The utility consumption guarantees
- A list of the accepted test procedures that will be used
- The guarantee test run procedures which are written in some detail
- Description of the notices to be given in the event the guarantees are not met

These items are described and discussed in Chapter 17 and an example of both the performance guarantee and its associated utility guarantee is given in Appendix 17.9 of this Chapter.

Process configurations

Process configurations are represented in the form of block flow diagrams. They are prepared usually as the first step in deciding the type of process units that will make up a desired complex. These units are shown in sequence to each other by blocks which will be labeled with their throughput size (in the case of a petroleum refinery in barrels per stream day or in cubic meters per stream day). The diagram is further developed showing the product and feed lines from and to the unit blocks. The measure of flow is shown on each line. This will be in terms of barrels per calendar day or cubic meters per calendar day. Several block flow diagrams of differing configurations but meeting the end product objectives will be developed prior to the decision as to which route meets all the company's objectives. A simplified block flow diagram is shown as Figure 19.P.1.

Each of these process configurations will be cost estimated to provide a comparative capital or installed cost, their operating costs, and the refinery price for products

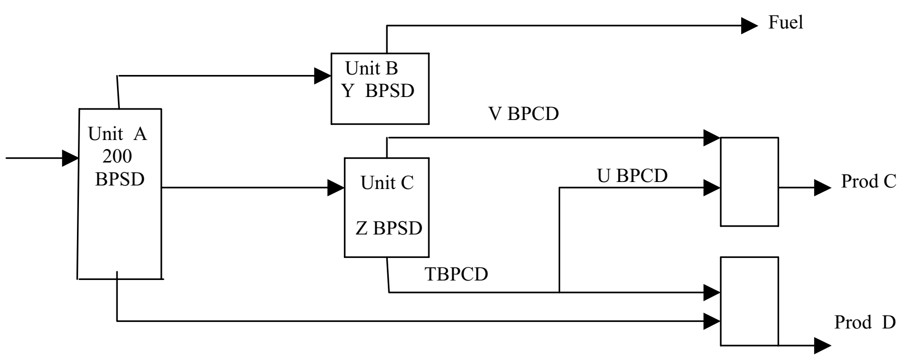


Figure 19.P.1. A typical block flow diagram.

and feedstock. With these parameters an economic evaluation to determine the best configuration can be made using the company's accepted evaluation procedures or by linear programming using a computer. Details of the development of a process configuration is given in Chapter 2. The use of process configuration in economic evaluation is described and discussed in Chapter 17. The sequence of events using process configurations that leads to a decision making item is given in Chapter 17 as Figure 17.3.

Project duty specification

Among the first activities to initiate a refinery project is the development of the "Project Duty Specification". This document must describe in detail the plant or complex of plants the company wishes to build. Among the major items of the Project Specification are:

The process specification
General design criteria
Any preliminary flow sheets (duly labeled "Preliminary")
Utilities specification
Basis for economic evaluations
Materials of construction
Equipment standards and codes
Instrument standards required

These items are described in detail in Chapter 17.

When completed and approved, the duty specification will form part of the enquiry document soliciting competitive bids from suitable contracting companies. More importantly it will form part of the contract awarded to the successful contractor. It will be accompanied in both the enquiry document and the contract with a detail of the contractor's scope of work, type of contract (i.e., Cost Plus, Lump Sum, etc.), guarantees required and other contractual items, including progress reports and meetings, approval requirements, etc.

Product blending

Finished products are blended with two or more components which are run down stream products from the refinery processes. The blending in most modern refineries is done "In Line". That is to say that measured amount of each component are mixed together in the line that finally enters the respective finished product storage tanks. The flow of each of the components is controlled 'on line' by analyzers which are programmed to open or close the component flow control valves to meet the specified

product blend recipes. Although these analyzers are quite accurate the final contents of the finished tanks are always checked by laboratory tests before dispatch out of the refinery. Sufficient room is left in the finished tank to allow correction if this becomes necessary. Gasolines are always checked for octane number, Reid vapor pressure and volatility. Kerosenes are checked for flash point, and volatility. Aviation gasolines are subjected to much more stringent properties which would include water content, vapor pressure, and sulfur content. Gas oils (including diesel) are checked for diesel index, sulfur content, pour point, viscosity, and flash point. Fuel oils are tested for viscosity, sulfur content, flash point, and pour points. All finished products are tested for specific gravity. Chapter 2 describes and discusses the product properties. This chapter also illustrates the blending recipes in a typical process configuration.

Pseudo components

This subject has been described earlier under the item predicting product properties.

Pumparound

This is the term given to any reflux stream which is created inside the distillation tower by taking off a hot liquid stream, cooling it, and returning the stream back into the tower two or three trays above the draw off tray. The following Figure 19.P.2 shows a typical pumparound system.

Pumparound systems are usually associated with complex distillation processes such as the atmospheric and vacuum crude oil distillation, where a single reflux stream (i.e., overhead condensate) would result in too low a reflux in the lower section of the tower. A single overhead reflux also would require a large tower diameter to cater for

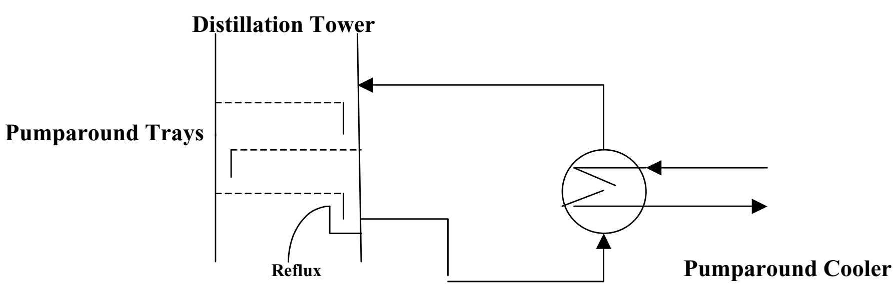


Figure 19.P.2. A typical pumparound arrangement.

the increased tower vapor and liquid traffic. The pumparound concept does smooth out the liquid/vapor traffic in the whole tower. The highest try loading in any distillation tower is below the bottom reflux stream. The addition of a pumparound therefore becomes a prime choice for a study to increase the distillation tower capacity on a revamp project.

Pumps

Types of pumps

Pumps in the petroleum and other process industries are divided into two general classifications which are

- Variable head-capacity
- Positive displacement

The variable head capacity types include centrifugal and turbine pumps whilst the positive displacement types cover reciprocating and rotary pumps. A summary of these types is as follows:

Centrifugal pumps. Centrifugal pumps comprise of a very wide class of pumps in which pumping of liquids or generation of pressure is effected by a rotary motion of one or several impellers. There are no valves in centrifugal type pumps (except of course, isolation valves). Flow is uniform and devoid of pulsation.

Turbine pumps. Turbine pumps are a type of centrifugal pumps designed to recover power in systems of high flow and high differential pressure. These pumps transmit some of the kinetic energy in the fluid into brake horsepower. The actual energy recovery is about 50% of the hydraulic horsepower available. This type of pump is expensive and is therefore not as widely used as the centrifugal pump.

Rotary pumps. Rotary pumps are positive displacement pumps. Unlike the centrifugal type pump these types do not throw the pumping fluid against the casing but push the fluid forward in a positive manner similar to the action of a piston. These pumps however do produce a fairly smooth discharge flow unlike that associated with a reciprocating pump. The types of rotary pumps commonly used in a process plant are:

Gear pumps
Screw pumps
Lobular pumps
Vane pumps

Reciprocating pumps. These are positive displacement pumps that use a piston within a fixed cylinder to pump a constant volume of fluid for each stroke of the piston. The discharge from reciprocating pumps is pulsating. Reciprocating pumps fall into two general categories. These are the simplex type and the duplex type. In the case of the simplex pump there is only one cylinder which draws in the fluid to be pumped on the back stroke and discharges it on the forward stroke. External valves open and close to enable the pumping action to proceed in the manner described. The duplex pump has a similar pumping action to the simplex pump. In this case however there are two parallel cylinders which operate on alternate strokes to one another. That is when the first cylinder is on the suction stroke the second is on the discharge stroke.

Other positive displacement pumps. There are other positive displacement pumps commonly used in the process industry for special services. Some of these are:

Metering or proportioning pumps—Which are small reciprocating plunger type pumps with an adjustable stroke.
Diaphragm pumps—These pumps are used for handling thick pulps, sludge, acid or alkaline solution, and fluids containing gritty solid suspensions. These are not usually used in petroleum refining.

Characteristic curves. Pump action and the performance of a pump are defined in terms of their *Characteristic Curves.* These curves correlate the capacity of the pump in unit volume per unit time versus discharge or differential pressures. Typical curves are shown in Figures 18.13–18.15 of Chapter 18.

Figure 18.13 is a characteristic curve for a reciprocating simplex pump which is direct driven. Included also is this reciprocating pump on a power drive.

Figure 18.14 gives a typical curve for a rotary pump. Here the capacity of the pump is plotted against discharge pressure for two levels of pump speed. The curves also show the plot of brake horsepower versus discharge pressure for the two pump speed levels.

Figure 18.15 is a typical characteristic curve for a centrifugal pump. This curve usually shows four pump relationships in four plots. These are:

- A plot of capacity versus differential head. The differential head is the difference in pressure between the suction and discharge.
- The pump efficiency as a percentage versus capacity.
- The brake horsepower of the pump versus capacity.
- The net positive suction head (NPSH) required by the pump versus capacity. The required NPSH for the pump is a characteristic determined by the manufacturer.

Detailed description and definition of terms associated with refinery pumps are given in Chapter 18. The chapter also describes the various pump drivers and supports these descriptions and discussions with worked examples. Finally the chapter gives the contents of a typical process specification for a centrifugal pump.

R

Reboilers

Reboilers are one of two heat energy input systems to a fractionation unit. The other source is the heat delivered by the feed or feeds to the unit. Reboilers are usually associated with the light ends distillation units and the product stabilizers and splitters on catalytic or thermal cracking units. In most cases, the reboiler is of a shell and tube type or a kettle type. In certain cases a fired heater may be used as a reboiler. This unit is fed either by the liquid phase from the bottom tray of the tower, or by vaporizing a portion of the bottom product. The first method uses thermosyphon as the driving force for flow through the heat exchanger. In the second case, the reboiler feed may be pumped or flow into the kettle section of the exchanger. In both cases, the flow from the reboiler is returned to the tower below the bottom fractionating tray. These two types are shown in Figure 19.R.1.

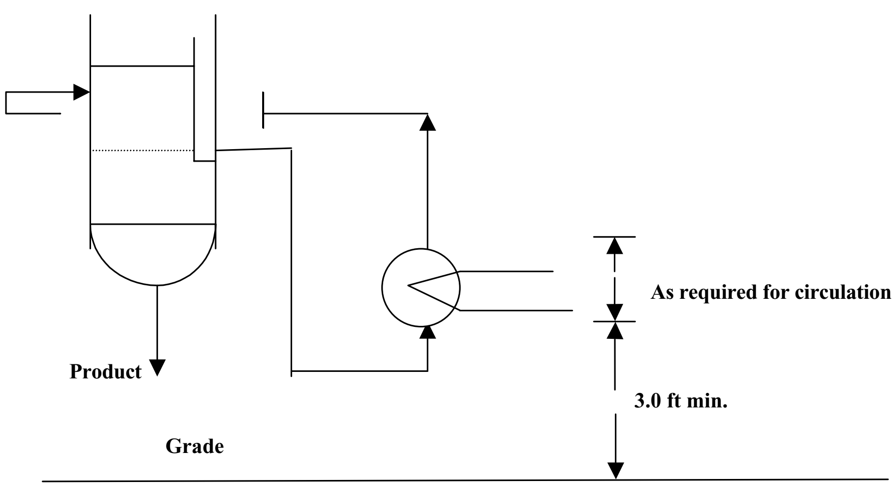


Figure 19.R.1. A once through thermosyphon reboiler.

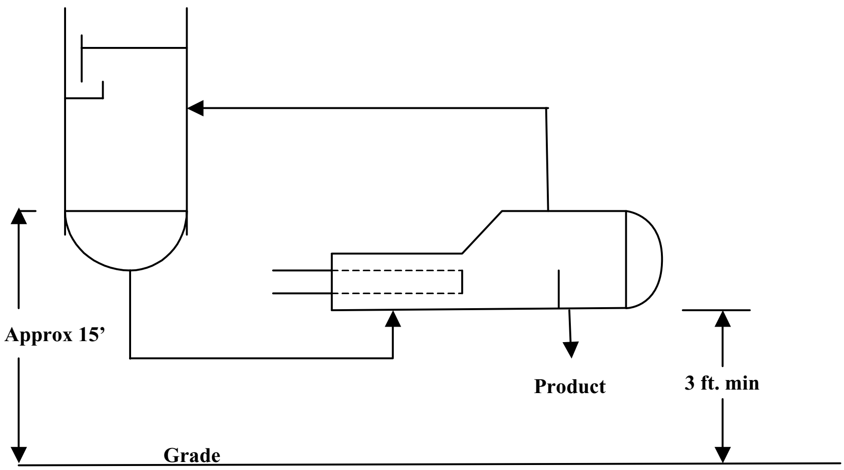


Figure 19.R.2. A kettle type reboiler.

There are two other types of reboilers used in the petroleum industry. These are the recirculating thermosyphon and the fired heater reboiler. Details of all types of reboilers are given in Chapter 18.

This chapter also discusses the operation of the reboilers with respect to their production of vapor and liquid flow objectives, which are:

1. To provide sufficient vaporising in the tower to strip the bottom product effectively.
2. To establish the loading on the bottom tray (and section) of the tower.
3. To establish the driving force for flow through the exchanger in the case of thermosyphon reboilers.

A typical bottom of the tower calculation is provided as an example. The heating medium for the heat exchange reboilers may be a hot process stream, or steam at an appropriate temperature and pressure level.

Reciprocating compressors

Reciprocating compressors are widely used in the petroleum and chemical industries. They consist of pistons moving in cylinders with inlet and exhaust valves. They are cheaper and more efficient than any other type in the fields in which they are used. Their main advantages are that they are insensitive to gas characteristics and they can handle intermittent loads efficiently. They are made in small capacities and are used in applications where the rates are too small for a centrifugal. Reciprocating compressors are used almost exclusively in services where the discharge pressures

are above 5,000 PSIG. However, when compared with centrifugal compressors, the reciprocating compressors require frequent shutdowns for maintenance of valves and other wearing parts. For critical services, this requires either a spare compressor or a multiple compressor installation to maintain plant throughput. Chapter 18 describes and discusses reciprocating compressors in detail. The chapter includes discussion on the compressors ancillary equipment such as inter stage coolers, valve lifters, and compressor control in general. Table 18.22 in this chapter lists the services for which the various types of compressors are used. It also provides calculation procedures with example calculation for determining the compressor characteristics such as horsepower, suction, and discharge conditions, etc. Finally the chapter provides the input required in a typical process specification for a reciprocating compressor.

Refineries

Most of this work is devoted to the energy refinery. That is the refinery that converts the crude oil feed to energy products such as gasoline, diesel, aviation turbine gasoline, fuel oil, and the like. There are two major refinery complexes however that convert the crude oil into non-energy products. These are the lube oil refinery and the petrochemical refinery. Very often these complexes are located adjacent to the energy refinery and they are often integrated into one major refinery complex. Chapter 12 describe and discuss these two refinery complexes. They are also summarized in the introduction in Chapter 1.

The lube oil refinery

The process configuration for a typical lube oil refinery is given in Chapter 1 as Figure 1.13. Briefly, the light vacuum distillate from the crude vacuum distillation unit is routed to a secondary vacuum distillation unit where a light and heavy spindle oil cuts are removed as distillate and light motor grade oil as residue. Both the motor oil and heavy spindle oil are hydrotreated in blocked operation. The light and hydro treated heavy spindle oils, with a portion of the motor oil enter the spindle oil pool. The remainder of the motor oil is routed to the light engine lube pool. The medium vacuum gas oil distillate from the crude oil vacuum distillation unit is routed directly to a de-waxing unit (in this case a methyl ethyl ketone process). A portion of the de-waxed product is routed to the light engine oil pool while the remainder enters the heavy engine oil pool. The heavy vacuum gas oil cut from the vacuum unit is treated in the fufural extraction unit for the removal of the heavy olefin components before entering the de-waxing plant operating on a blocked operation. The de-waxed product from this operation is divided between the heavy engine oil pool and the turbine lube oil pool. The residue from the crude oil vacuum unit is de-asphalted in a propane de-asphalting unit. (Note: There are other de-asphalting processes but propane de-asphalting is the most common). The de-asphalted oil from this unit is

called 'Bright Stock' and its processing follows that of the heavy vacuum gas oil, again on a blocked operation. After fufural extraction and dewaxing the bright stock is routed to the turbine lube oil pool.

Finally a portion of the vacuum residue is routed directly to the bitumen blending pool bypassing the PDA (propane de-asphalting) unit. A portion of the extracted asphalt stream from the PDA unit is routed to a bitumen blowing unit while the remainder joins the vacuum residue in the bitumen blending pool. The blown bitumen is the third stream that enters the bitumen blending pool. The various blended grades of bitumen are routed to storage and packaging. The base stocks of the turbine, engine oils, and spindle oils are sent to blending and packaging for further preparation of the respective commercial products ready for dispatch.

The petrochemical refinery

A configuration for a typical petrochemical refinery is given in Chapter 1 and shown as Figure 1.14 in that chapter. This configuration confines itself to the production of the olefin feedstock following steam cracking of a feedstock consisting of light atmospheric crude oil distillate, a naphtha cut, and the light distillate from a hydro-cracker. The refineries aromatic product stream is produced in a conventional catalytic reformer operating with a blend of straight run naphtha and hydro-cracker naphtha as feedstock. This reformate product enters an aromatic extraction unit where an aromatic rich stream leaves as the product. This configuration shows a coking unit taking the vacuum crude distillation residue as feed. The main purpose of this unit in the configuration is to provide increased feed to the hydrocracker and thus additional naphtha to the reformer and steam cracker. Other residue conversion units may be considered as an alternate to the coking unit, such as 'Deep Fluid Cracking' unit, or a residue hydrocracking unit.

Reformulated gasolines

The requirements of the clean air act of 1990 and additions to it since have changed refining requirements to meet this product's need quite significantly. Prior to this date much of the gasoline finished product recipe consisted of normal light naphtha, a reformate, usually some cracked naphtha and possibly an alkylate, with some butane added to meet volatility. The clean air requirement and its subsequent additions forced a reduction of both the reformate and the cracked stock and to replace them with oxygenates such as MTBE and TAME to meet octane number. Oxygenates were used originally simply as a additive to improve octane number. However, because of their oxygen content their addition was also required to reduce the carbon monoxide and hydrocarbons in the emission gases. There are a number of oxygenates used in gasoline manufactures; some of the more common are given in the following Table 19.R.1.

Table 19.R.1. Oxygenates commonly used in gasoline

Name	Formula	RON	RVP psig	Oxygen wt%	*Water solubility %
Methyl tertiary butyl ether (MTBE)	$(CH_3)_3COCH_3$	110–112	8	18	4.3
Ethyl tertiary butyl ether (ETBE)	$(CH_3)_3COC_2H_5$	110–112	4	16	1.2
Tertiary amyl methyl ether (TAME)	$(CH_3)_2(C_2H_5)COCH_3$	103–105	4	16	1.2
Ethanol	C_2H_5OH	112–115	18	35	100

*wt% soluble in water.

The EPA established limits for the use of each oxygenates in gasoline blends. For example, MTBE could be blended up to 15 vol% subject to an overall limit of 2.7 wt% oxygen content. The role of MTBE and other oxygenates was reviewed in the late 1990s after it was discovered that underground storage tanks had not been upgraded to retain reformulated gasoline. As a consequence tanks were leaking gasoline that contained MTBE into the ground and drinking water systems. Therefore, use of MTBE in the U.S. was essentially discontinued by the end of 2002. MTBE is still widely used outside the U.S. although the trend in western Europe is to use ETBE instead. More details on the manufacture of gasolines are given in Chapter 2.

Reid vapor pressure

This test is the standard test for low boiling point distillates. It is used for naphtha, gasoline, light cracked distillates, and aviation gasoline. For the heavier distillates with vapor pressures expected to be below 26 psig at 100°F the apparatus and procedures are different. Only the Reid vapor pressure for those distillates with vapor pressures above 26 psig at 100°F are described in Chapter 16. The apparatus used for this test is given as Figure 16.5.

Relief valves

Full details and discussion on relief systems which include the relief valves used in the petroleum industry are given in Chapter 13. The following is a list of those types of relief valves commonly used in industry. These have been approved according to ASME V111 “Boiler and Pressure Vessel” code:

Conventional safety relief valves

In a conventional safety relief valve the inlet pressure to the valve is directly opposed by a spring closing the valve, the back pressure on the outlet of the valve changes the

inlet pressure at which the valve will open. A diagram of a conventional relief valve is shown in Chapter 13 as Figure 13.37.

Balanced safety relief valves

Balanced safety valves are those in which the back pressure has very little or no influence on the set pressure. The most widely used means of balancing a safety relief valve is through the use of a bellows. In the balanced bellows valve, the effective area of the bellows is the same as the nozzle seat area and back pressure is prevented from acting on the top side of the disk. Thus the valve opens at the same inlet pressure even though the back pressure may vary. A diagram of a balanced safety relief valve is shown in Chapter 13 as Figure 13.38.

Pilot operated safety relief valves

A pilot-operated safety relief valve is a device consisting of two principal parts, a main valve and a pilot. Inlet pressure is directed to the top of the main valve piston, and with more area exposed to pressure on the top of the piston than on the bottom; pressure, not a spring, holds the main valve closed. At the set pressure the pilot opens reducing the pressure on top of the piston and the main valve goes fully open.

Resilient seated safety relief valves

When metal-to-metal seated conventional or bellows type safety relief valves are used where the operating pressure is close to the set pressure, some leakage can be expected through the seats of the valve (Refer to API Standard 527, “Commercial Seat Tightness of Safety Relief Valves with Metal-to-Metal Seats”).

Rupture disk

A rupture disk consists of a thin metal diaphragm held between flanges. The disk is designed to rupture and relieve pressure within tolerances established by ASME Code.

Residue conversion units

The conversion of residues to more commercially attractive products is described and discussed in Chapter 11. The processes addressed in this context are:

Thermal cracking
‘Deep oil’ fluid catalytic cracking
Residuum hydro cracking and desulfurization

Thermal cracking

The thermal cracking processes refer to those that convert the residuum feed (whether atmospheric or vacuum residues) into higher grade products such as naphtha and middle distillates, by heat at high temperature alone. That is, no catalyst or chemicals are used in the conversion. The processes themselves are:

Visbreaking
Thermal cracker
Cokers

Certain confusion exists in the definition of visbreaking and thermal cracking. Differentiation is based on the type of feedstock, severity of cracking or the final result. Strictly speaking, the term visbreaking should refer only to the viscosity reduction of heavy stock as the process main objective.

A residue feed stream (either from the atmospheric tower or the crude vacuum tower), is cracked in a specially designed heater. The effluent from the heater is quenched and routed to a fractionator, sometimes with a pre-flash. The products of cracking such as light gases, naphtha, gas oil, and residue are separated in the conventional manner. Some 20% of the residue feed can be converted into lighter products, mostly gas oil, by this process. Figure 11.1 of Chapter 11 shows a typical one stage thermal cracker. A visbreaker unit would have the same process configuration but the temperature severity and residence time in the heater would be less stringent than that required for product up grading.

There are two coker processes: the delayed coker, and the fluid coker. In the delayed coker the residuum feed is heated to above its dissociation temperature in a fired heater. Some coke is formed in the heater but the major portion of the coke is formed in the large drum to which the heater effluent is routed. The hot effluent is retained in this drum for a specified period of time (in some cases 8–12 hr). The liquid phase is drawn off slowly leaving the coke to remain in the drum. At the end of the specified period or when the drum is full, the coke is cooled and removed using high-pressure water jets.

Most present day fluid-coking units use a proprietary process licensed by Exxon called Flexi-Coking. Briefly, this process is an extension of the traditional fluid-coking process. The extension allows for the gasification of the major portion of the coke make to produce a low Btu gas.

Heavy residuum feed is introduced into the reactor vessel where it is thermally cracked. The heat for cracking is supplied by a fluidized bed of hot coke transferred to the reactor from the heater vessel. The vapor products of the reaction leave the reactor zone to enter the product recovery section consisting of a scrubber and a conventional

fractionating facility. Steam is introduced to the bottom of the reactor to maintain a fluid bed of coke and to strip the excess coke leaving the reactor free from entrained oil.

The coke leaving the reactor enters the heater vessel, where some of the coke is converted into CO/CO_2 in the presence of air. This conversion of the coke provides the heat for cracking which is subsequently transmitted to the reactor by a hot coke stream. The net coke make leaves the heater and enters the gasifier vessel. Air and steam are introduced into the gasifier to react with the coke producing a low Btu gas consisting predominately of hydrogen, CO, CO_2, and nitrogen. This gas together with some excess air is transferred to the heater, and leaves this vessel to be suitably cleaned and cooled.

Both the delayed coker and the flexi-coker are described and discussed in Chapter 11 with process configuration drawings shown as Figures 11.4 and 11.5 in that chapter.

Deep oil cracking

This process is a form of the traditional Fluid Catalytic Cracking Process (FCCU). Originally FCC was restricted in the type of feedstock it could handle and one of the major constraints in this respect was the Conradson carbon contents of the feed. Even for the processing of distillate it had to be below 10 ppm. There were other constraints such as metal content that made the processing of residuum impossible. However in the late 1980s with a much improved catalyst and minor modification to the process configuration it became feasible to process most residues, including vacuum residue in the so-called "deep catalytic cracking" unit, or DC Full details of this process and discussion are given in Chapters 5 and 11. These chapters also contain process diagram of deep oil cracking process.

Residue hydrocracking

The most common hydro-cracking process for residue conversion is the fixed catalyst bed process. There is also a process that utilizes an ebullated catalyst bed but only the fixed bed process is described in Chapter 11. A typical process diagram for a complex utilizing the hydrocracker coupled with a thermal cracker or visbreaker is shown as Figure 11.15. Bitumen feed from the crude vacuum distillation unit enters the hydrocracker section of the plant to be preheated by hot flash vapors in shell and tube exchangers and finally in a fired heater. A recycle and make up hydrogen stream is similarly heated by exchange with hot flash vapors. The hydrogen stream is mixed with the hot bitumen stream before entering the hydrocracker heater. The feed streams are preheated to the reactor temperature in the fired heater and enter the top of the

reactor vessel. The feed streams flow downwards through the catalyst beds contained in the reactor.

The reactor effluent leaves the reactor to enter a hot flash drum. Here the heavy bituminous portion of the effluent leaves from the bottom of the drum while the lighter oil and gas phase leaves as a vapor from the top of the drum. This vapor is subsequently cooled by heat exchange with the feed and further cooled and partially condensed by an air cooler. This cooled stream then enters a cold separator operating at a pressure only slightly lower than that of the reactor. A rich hydrogen gas stream is removed from this drum to be amine treated and returned as recycle gas to the process. The distillate liquid leaves from the bottom of the separator to join a vapor stream from the hot flash surge drum (thermal cracker feed surge drum). Both these streams enter the cold flash drum which operates at a much lower pressure than the upstream equipment. A gas stream is removed from the drum to be routed an absorber unit. The liquid distillate from the drum is routed to the de-butanizer in a light ends recovery unit and subsequently the product recovery process.

Residues

In petroleum refining the term 'Residue' refers to the un-vaporized portion of the heated crude oil entering either the atmospheric crude oil distillation tower or vacuum tower that leaves these towers as their bottom product. The stream from the atmospheric column is often referred to as the 'long' residue while that from the vacuum unit is often called the 'short' residue or bitumen. Both residues are black in color the atmospheric residue has a specific gravity usually between 0.93 and 0.96, whist the vacuum residue will be 0.99 and higher.

Road and rail loading facilities

Please refer to the item offsites in this chapter and Chapter 13.

S

Safety systems

The most hazardous occurrence in any oil refinery or really any establishment that handles hydrocarbons is that of a fire. Because of this, considerable emphasis in the safety policy of these plants is geared to fire prevention and fire fighting.

The fire safety measures are more important perhaps in oil refining than any other related facility because of the relative size of most refineries compared with petrochemical or chemical facilities. Refinery prevention and protection begins at the early stages of the refinery design and engineering. Chapter 6 details the development of the fire prevention and fire fighting through the early stages of the refinery design in describing the relevant passages that are usually contained in the project design specification. There are engineering and design standards that contractors must adhere to. They include the standards for mechanical equipment, electrical equipment (such as the 'Area Classification Code' which sets the parameters for equipment in terms of fire proofing (i.e., whether the item is to be spark proof, etc.) that will be located in the various areas of the refinery. The piping and layout specification will detail the piping codes to be used and the material break points. It will proceed to establish the criteria for equipment and tankage layout with respect to fire prevention (e.g., distance of fired heaters from other equipment). Other design specifications include amongst other requirements, fire prevention equipment such as sprays to be located on storage tanks, and vessels. Finally this Chapter 6 describes the location, size, and operation of refinery fire mains. On large installations these could amount to three or more separate fire main loops remotely and centrally controlled and operated.

Other safety systems that are part of petroleum refining concern the handling of hazardous chemicals. The item in Chapter 6 covers some of these compounds as to their storage and handling in the refinery. The chemicals selected as the most hazardous usually met with in the refining processes are: AHF (anhydrous hydrofluoric acid), amines, furfural, hydrogen sulfide, and MEK (methyl ethyl ketone). The composition of each of these chemicals is described, together with their injurious effect on humans and the remedial procedures to be adopted in the event of an accident. The chapter continues with a review of the materials of construction for these chemicals and the protective clothing that should be worn when handling them. The fire hazards of these chemicals are also highlighted.

Side stream stripping

Side streams from multi-component distillation towers are stripped free of entrained lighter products. Stripping may be accomplished either by injection of steam through the hot side-stream in a trayed column, or by injection of an inert gas instead of steam, or by reboiling the bottom product of the stripper tower. By far the most common method is that of steam stripping and the most common application is on the atmospheric crude distillation unit. Figure 19.S.1 shows the bottom distillate side stream stripper of a crude distillation unit.

Each side stream draw off from the main tower would be stripped free of entrained light ends in similar trayed columns. Normally these side stream columns would

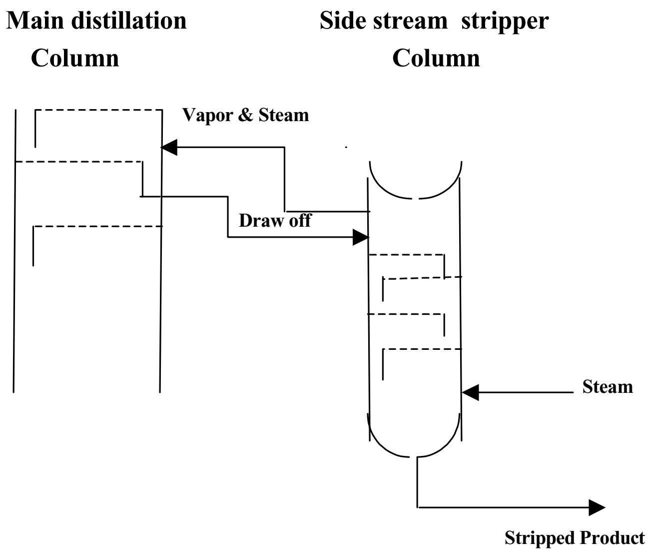


Figure 19.S.1. Side stream steam stripper.

be stacked to provide a single stripping tower. Such an arrangement is shown in Chapter 3 Figure 3.2. This chapter also describes the side stream stripper function with example calculations. It also provides recommended steam rates for the various stripping functions.

Soaking volume factor

The design of a thermal cracker is keyed to the configuration and temperature profile across the heater and soaking drum or soaking coil. The degree of cracking is dependant on this temperature profile and the residence time of the oil under these conditions. The soaking volume factor (SVF) is related to product yields and the degree of conversion. Definition of these items are given in Chapter 11. A design calculation using the SVF (soaking volume factor) is given as Appendix 1 of this chapter.

Specific gravity

The specific gravity of a liquid is the weight of a known volume of the liquid at a known temperature compared with water under the same conditions. The standard weight is taken as one gram and the standard temperature is usually 60°F or 15°C. The specific gravity of a petroleum compound is the basis for development of the material balance in design work, and most measurements within the refinery.

The basic specific gravities are given as an essential part of the crude assay. They are usually presented as a curve of specific gravities (usually quoted as °API) against mid point distillation temperatures. API gravities are related to specific gravities by the equation: specific gravity $= 141.5/(131.5 + {}^{\circ}\mathrm{API})$. The specific gravity of any petroleum compound may be calculated using the method provided in Chapter 1. The specific gravity of crude oil and its products are obtained in the refinery using the test method described in Chapter 16. The method uses a properly calibrated hydrometer under laboratory conditions.

Splitter, naphtha

In all hydro skimming refineries the key process, next to the crude distillation process is the catalytic reformer. The correct design and subsequent operation of this process produces the hydrogen stream that is required by many refinery operations. Important to the efficient operation of this process is the correct boiling point range of the naphtha feed. This is ensured by the fractionation of the full range naphtha stream from the crude unit overhead distillate. This is accomplished as part of the light ends unit complex. Typically the total overhead distillates plus in some cases other naphtha distillates (from thermal crackers) are first de-butanized in the light ends de-butanizer column. The bottom product from this column is the de-butanized full range naphtha. This stream is delivered hot to a naphtha splitter fractionator which produces a light naphtha overhead and a heavy naphtha the bottom product. The fractionation between these two products maximizes the naphthene content of the heavy naphtha. As this heavy naphtha is fed to the catalytic reformer the amount of naphthenes in its composition will, to large extent, determine the amount of hydrogen the unit will produce. Splitter towers contain between 25 and 35 actual distillation trays and operate at overhead reflux ratios of between 1.5 and 2.0. Further details and description is given in Chapter 4.

Stacks

Stacks are used to create an updraft of air from the firebox of a heater. The purpose of this is to cause a small negative pressure in the firebox and thus enable the introduction of air from the atmosphere. This negative pressure also allows for the removal of the products of combustion from the firebox. The stack therefore must have sufficient height to achieve these objectives and overcome the frictional pressure drop in the firebox and the stack itself.

The height required for a stack to achieve good draft can be estimated from the following equation:

$$\mathrm{D} = 0.187\,\mathrm{H}\,(\rho_{\mathrm{a}} - \rho_{\mathrm{g}})$$

where

D = draft in ins of water.
H = stack height in feet.
ρ_a = density of atmospheric air in lbs/cuft.
ρ_g = density of stack gasses in lbs/cuft at stack conditions.

For stack gas temperature use 100°F lower than gases leaving the convection section. Stack gasses are mostly nitrogen with some CO_2 with an average molecular weight of about 28. Details on stacks including velocity head, emissions, and environmental considerations are given in Chapter 18.

Steam and condensate systems

In most plants, steam condensate accumulated in the various processes is collected into a single header and returned to the boiler or steam generating plant. It is stored separate to the treated raw water because condensates may contain some oil contamination. A stream of treated water and condensate are taken from the respective storage tanks and pumped to the deaerator drum. The condensate stream passes through a simple filter on route to the deaerator to remove any oil contamination. Low-pressure steam is introduced immediately below the packing in the deaerator to flow upwards countercurrent to the liquid streams to remove any entrapped air in the liquid. The deaerated boiler feed water (BFW) is pumped by the boiler feed water pumps into the steam drum of the steam generator. There will normally be three 60% pumps for this service. Two will be operational and one will be on standby. These pumps are the most important in any chemical plant or a petroleum refinery. If they fail no steam can be generated and the whole complex is in danger of total shutdown or worse. Therefore, three separate pumps are used to cater for the normal high head and high capacity, and a separate pump driver operating on a completely different power source than electrical power or steam (usually a diesel engine) is mandatory for atleast one of the pumps to minimize the danger of complete shut down.

The steam drum is located above the generator firebox. The liquid in the drum flows through the generator coils located in the firebox by gravity and thermo-syphon. A mixture of steam and water is generated in the coils and flows back to the steam drum. Here, the steam and water are separated with the steam leaving the drum to enter the super-heater coil. This coil located in the lower section of the convection side of the heater super heats the saturated steam to the high-pressure refinery steam mains. Let down stations may be located at various points in the refinery to create lower pressure main systems. De-super heaters are used to establish the correct temperature levels in these lower pressure mains. Chapter 13 gives details of a steam generation

systems and condensate recovery. Figure 13.27 provides a schematic diagram of a steam generation plant.

Storage facilities

Please refer to the item in Part 2 Offsites and Chapter 13.

Sulfur removal

Naphtha desulfurization

This uses catalytic ("cat") reformer hydrogen on a once through basis. Heavy naphtha feed to the cat reformer is fed to the naphtha hydrofiner from storage. The feed stream and the hydrogen gas stream are pre-heated by exchange with the hot reactor effluent stream. The feed then enters the fired heater which brings it up to the reactor temperatures (about 450°F) and leaves the heater to enter the reactor which operates at about 400–450 psig. Sulfur is removed from the hydrocarbon as hydrogen sulfide in this reactor and the reactor effluent is cooled to about 100°F by heat exchange with the feed. The cooled effluent is collected in a flash drum where the light hydrogen rich gas is flashed off. This gas enters the suction side of the booster compressor which delivers it to other hydrotreaters. The liquid phase from the drum is pumped to a reboiled stabilizer. The overhead vapor stream from the stabilizer is routed to fuel while the bottom product, cat reformer feed, is pumped to the cat reformer.

Gas oil desulfurization

This process uses a recycled hydrogen stream to desulphurise a gas oil feed. Figure 19.S.2 shows the gas oil feed entering the unit to be pre-heated with hot effluent stream before entering a fired heater. Where its temperature is increased to the reactor temperature of about 750°F. A hydrogen rich stream is introduced at the coil outlet prior to the mixed streams entering the reactor. The reactor contains a bed of cobalt molybdenum on alumina catalyst and desulfurization takes place over the catalyst with 70–75% of the total sulfur in the oil being converted to H_2S.

The reactor effluent is cooled by the cold feed stream, water or air. This cooled effluent enters a flash drum where the gas phase and liquid phase are separated. The gas phase rich in H_2S and hydrogen enters the recycle compressor. The gas stream then enters an amine contactor where the H_2S is absorbed into the amine and removed from the system. Although the diagram shows a purge stream before the amine absorber in most cases the purge is downstream after the amine cleanup. The purged gas is

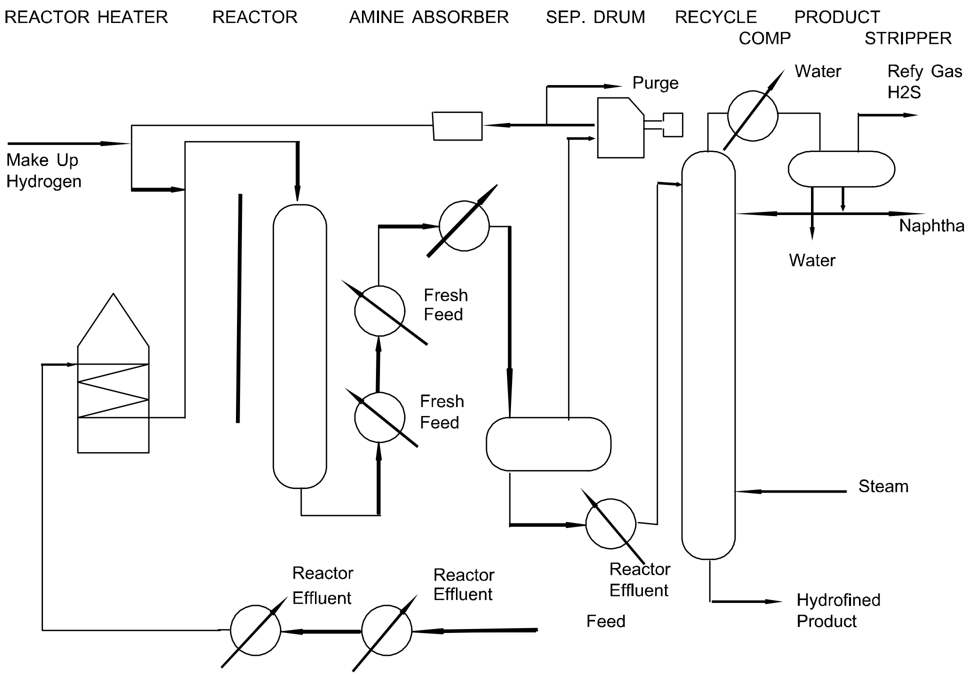


Figure 19.S.2. A typical middle distillate desulfurizer.

replaced by fresh hydrogen-rich make-up, thus maintaining the purity of the recycle gas.

The liquid phase leaving the flash drum is pre-heated before entering a stream stripping column where the light ends created in the process are removed as overhead products. The bottom product leaves the tower to be cooled and stored. Details of desulfurization of naphtha and heavier products are given in Chapter 8.

Other desulfurizing processes

Light naphtha and lighter hydrocarbons have sulfur content predominately in the form of mercaptans (see Chapter 1 for a definition of mercaptans.). These sulfur components are easily removed by a simple caustic wash or in licensed processes such as UOP's Merox process. Some refiners however elect to hydrotreat the debutanized full range naphtha before splitting the desulfurized product into the light and heavy product. Indeed several hydrotreat the whole of the crude unit overhead distillate, doing away with any further processing to eliminate the mercaptans. The problem here is however the loss of some LPG due to the high hydrogen content of the debutanizer overhead drum components.

At the other end of the crude oil product spectrum, in the area of the heavy vacuum gas oil and residue, desulfurization by hydrotreating requires a high severity operation. The reason for this is that the sulfur molecules in this case are in the form of thiophenes. These are sulfur molecules deeply encapsulated in the heavy hydrocarbon molecules. To expose the sulfur to the hydrogen stream requires some degree of cracking of the hydrocarbon molecule. Desulfurization in this case therefore becomes more of hydrocracking that hydrotreating.

Sulfur content

Sulfur content of a petroleum product or cut is always quoted as a percent by weight of the sample. The most common laboratory test for sulfur content is 'The Lamp Method ASTM D 1266' this is described in detail in Chapter 16. Briefly the test is as follows:

The sample is burned in a closed system using a suitable heat source and an artificial atmosphere of 70% carbon dioxide and 30% oxygen to prevent the formation of nitrogen oxides. The oxides of sulfur are absorbed and oxidized to sulfuric acid by means of a hydrogen peroxide solution. This solution is flushed with air to remove carbon dioxide. The sulfur as sulfate in the absorbent is determined by titration with standard sodium hydroxide. The calculation of the sulfur content from the titration is given by the following equation.

$$\text{Sulfur Content wt\%} = 16.03\,\text{M} \times (\text{A}/10\,\text{W})$$

where

A = milliliters of NaOH titrated
M = Molarity of the NaOH solution.
W = Grams of sample burned.

T

Tar

Tar is an ill-defined general term that describes heavy petroleum fractions that are solid or semi-solid at room temperature. An alternative term is *bitumen* although the latter is better used to denote naturally occurring tar deposits, as in tar pits or tar sands.

In addition to being very viscous or nonflowing materials (viscosity $>10{,}000$ cP), tars are also characterized by having relatively high densities lower than about 10 API degrees, which corresponds to a specific gravity (60/60) greater than 1.0.

$$\text{Degrees API} = \frac{141.5}{\text{sp. gr. at } 60^\circ\text{F}/60^\circ\text{F}} - 131.5$$

Depending on their physical properties, tars may be easily confused with asphalts. The main difference being that tars are usually either naturally occurring or unprocessed heavy fractions recovered as byproducts from other sources (e.g., petroleum residues or coal processing) while asphalts are typically processed or manufactured materials, whether air-blown or solvent extracted.

Sometimes, tars are further processed to recover the more volatile components. If so, the remaining very heavy residue is usually called *pitch* (1) (See also Chapter 12).

1. Gerd Collin, *"Tar and pitch." Ullmann's Handbook of Industrial Chemistry*, Wiley-VCH Verlag GmbH, 2002.

Tar sands

Tar sands or bituminous sands are several porous rock formations that contain highly viscous heavy hydrocarbon materials that cannot be recovered by conventional oil recovery methods, including enhanced oil recovery techniques. At present, the only practical method of recovering the hydrocarbons contained in tar sands is mining the tar sands followed by high-temperature retorting. Alternatively, in situ combustion or thermal processing techniques can be used to increase the fluidity of the hydrocarbons so as to enable their recovery out of the tar sands (1, 2).

Tar sands are characterized by having a relatively coarse porous structure. Some bituminous rock formations may, however, have a much tighter pore matrix that makes the recovery of the hydrocarbons even more difficult. An extreme case is evidenced in *oil shales* that are typically sedimentary clayish rock structures with a relatively high organic content (kerogen) that can be thermally decomposed to yield hydrocarbon-based oils. It is important to note that the hydrocarbons from oil shales, variously denoted as shale oils, cannot be recovered directly from the rock matrix, even using thermal means, but are only the products from the thermal decomposition of the kerogen. Often, shale oils have a relatively high nitrogen content that requires extensive hydrotreating before it can be used in standard petroleum refining applications.

Tar and shale deposits are extensively distributed worldwide and can potentially provide huge oil reserves for future generations. Some examples vary from the Brea tar pits in California, to the Athabasca tar sands in Canada, to the tar deposits in Trinidad or in the Orinoco river valley in Venezuela, to the tar deposits near the Caspian Sea, or to the shale oil deposits in Colorado and other parts in the western United States.

1. Frank J. Mink and Richard N. Houlihan, *"Tar sands." Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH, 2002.
2. R. W. Luhning, "Heavy oil, oil sands, and enhanced oil recovery: Where will the technology break-through come from?" Canadian Heavy Oil Association Conference on Heavy Oil—a New Direction, Calgary, Alberta, December 5, 1989.

Tetraethyl lead

A former additive used as an anti-knock additive to boost the octane number in gasoline. It was produced commercially from ethyl chloride. It was used at a dosage in 0–3 ml/gal range depending on the gasoline composition, sulfur content, and lead sensitivity. The use of tetraethyl lead has largely been discontinued worldwide, in particular as a result of the introduction of catalytic converters to clean up the exhaust from internal combustion engines. Use of lead irreversible poisons the oxidation catalysts used in such converters. Also, lead itself is a highly toxic substance that was present in automobile exhaust before it was banned with the advent of catalytic converters.

Other additives have been proposed or used to replace tetraethyl lead. Manganese derivatives (e.g., methyl cyclopentadienyl manganese tricarbonyl) were used for some time, principally in Canada. Methyl *tert*-butyl ether (MTBE) can be used both as an octane booster and as a gasoline pool extender, but MTBE has a foul smell and its use has fallen off in the United States as a result of ground water contamination from leaking gasoline tanks. It is, however, still used extensively in other countries along with ethyl *tert*-butyl ether (ETBE), and *tert*-amyl methyl ether (TAME). Passage of a legislatively mandated oxygenate requirement in the United States led to the increased usage of ethanol produced by the fermentation of grain, usually corn.

Thermal cracking

The earliest processing of crude oil involved its simple distillation (usually with batch stills) into various fractions that were variously called naphtha, kerosene, gas oil, etc. and with uses often limited to illumination and heating fuels. Neither the quantity nor the quality of the various fractions was particularly good. With the advent of

the earlier internal combustion engines it became apparent that the more desirable naphtha fraction yielded only a poor performance and its availability was very limited.

Thermal cracking was the first commercial process used for the conversion of petroleum fractions into more useful products. Though largely superseded by other processes (in particular catalytic cracking), thermal cracking was used for many years for the decomposition (cracking) of heavy, high-molecular weight hydrocarbons into smaller molecules, and is still used commercially in the processing of very heavy fractions, as in visbreaking or coking.

In a different sense, thermal cracking is also the technology that is used universally for the production of light olefins (ethylene to butenes, in particular) from hydrocarbon feedstocks that range from ethane, to LPG, to naphthas, and all the way to gas oils. Cracking for the production of olefins is a far more specialized technology that is practically the basis for the entire petrochemical industry.

Within the refinery environment, thermal cracking started as a batch process in the early 1900s. Crude oil was heated in a still; the different hydrocarbons vaporized according to their respective boiling points and were then condensed in separate fractions. Gasoline was in increasing demand but the amount recovered by batch distillation was only a small fraction of the crude fed to the still. A much larger portion remained in the still as a heavy material. William M. Burton of the Standard Oil Company is credited with having discovered thermal cracking by applying heat and pressure to decompose part of the residue remaining after gasoline had been boiled off. The result was that the yields of gasoline virtually doubled relative to those obtained by straight distillation. The early years of thermal cracking were mired in litigation resulting from the timing of the filings for intellectual property protection. While Burton was the first to intentionally crack heavy oil by thermal means, his patent application filed in the summer of 1912 came much later than a 1909 filing by J. A. Dubbs for a pipe still for the demulsification of oil that incidentally also resulted in some thermal cracking. These early Burton cracking stills suffered from significant coking problems; similar coking problems were also encountered in Dubbs's pipe stills but less so when used with the demulsification water. Both technical and legal issues were eventually resolved by Carbon Petroleum (C.P.) Dubbs, son of J. A. Dubbs who, together with Gustav ("Gasoline Gus") Egloff, developed a "clean circulation" continuous thermal cracking process that largely avoided the formation of undesirable coke deposits. The success of this process led to the licensing in 1919 of a first unit for the processing of 250 barrels/day to Roxana Petroleum Corporation, a Shell subsidiary, in Wood River, Illinois. By 1923, there were 65 new Dubbs units with total processing capacity of 42,000 barrels/day and by 1926 there were 107 producing units and another 37 under construction. The process was later improved and used extensively for many years throughout the world.

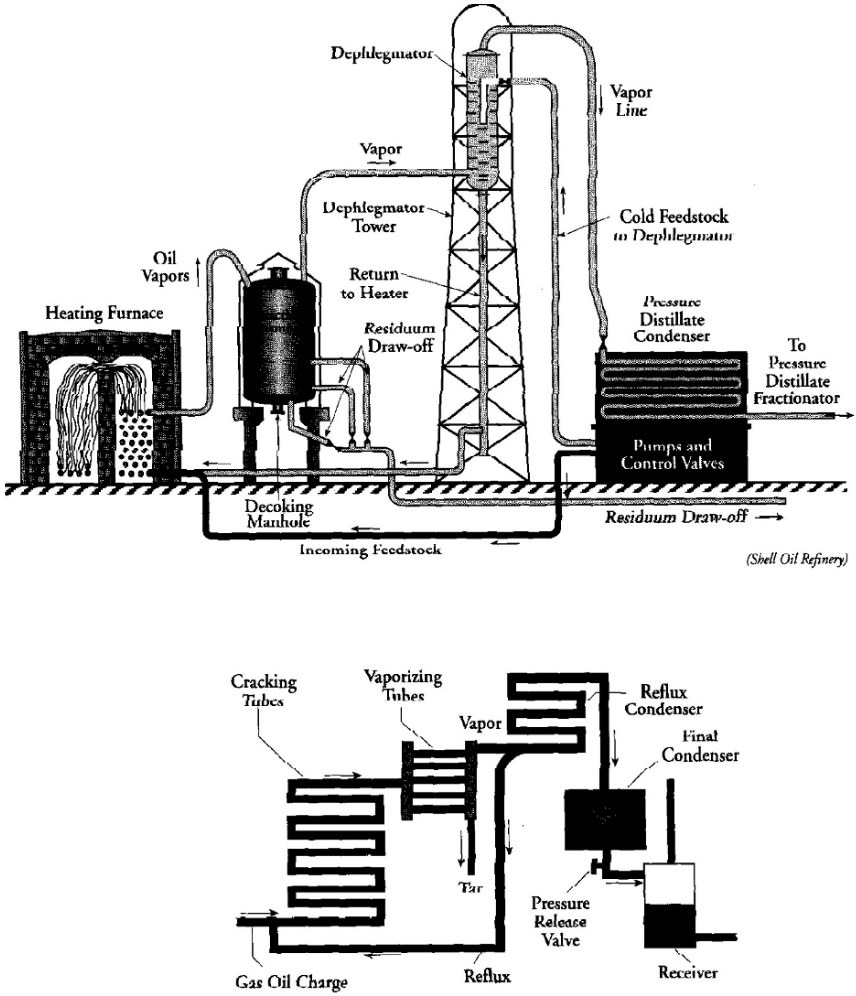


Figure 19.T.1. Flow schemes of the Dubbs circulation process.

Figure 19.T.1 illustrates a schematic of the Dubbs clean circulation process. The unit had four major components: a natural gas fired furnace where incoming oil was circulated through some 60 m of zig-zag tubes and heated to cracking temperature; an enlarged reaction chamber where the oil could remain or "stew" for a certain residence time and crack without providing additional heat; a dephlegmator where vapors from the cracked petroleum, including those of the gasoline product, could cool and partially condense before being separated; and a reflux line through which some of the heavier vapors that condensed in the dephlegmator could be rerouted

back to the feed line and mixed with fresh incoming oil. The recirculation of the clean material relative to the fresh “dirty” oil was done at about a three-to-one ratio. The small amount of coke that settled in the reaction chamber could be drained off continuously into separate tanks (see also Chapter 11).

Thermal reforming

Thermal reforming is similar to thermal cracking applied to gasoline boiling range hydrocarbons. Because of consisting of smaller molecules, they are more difficult to crack and require higher severities, with furnace outlet temperatures of up to about 600°C. Good per-pass conversions and good octane improvements can be obtained while coke formation is limited because of the lighter nature of the feedstock.

An excellent review of thermal processes, both cracking and reforming, can be found in the Petroleum Processing Handbook, edited by John J. McKetta, Marcel Dekker (1992).

To a large extent thermal reforming has been superseded by catalytic reforming and thermal cracking by fluidized catalytic cracking (FCC) except as outlined above.

Thermofor

“Thermofor” is the commercial name of a continuous moving bed process used either for catalytic cracking or catalytic reforming. A distinctive feature of this process is that the catalyst, usually chromia/alumina, flows down through the reactor concurrently with the hydrocarbons. A mechanical conveying system is used to circulate the catalyst back to the top of the reactors. (1)

1. James G. Speight and Baki Özüm, *Petroleum Refining Processes*, Marcel Dekker, 2002.

Topping

“Topping” or “skimming” is the name used for the distillation of crude oil to remove the lighter fractions. The crude oil with such fractions removed is sometimes called “topped crude.”

Crude oil is usually topped only down to some preselected intermediate temperature. The remaining heavy fraction may still contain substantial amounts of valuable intermediate hydrocarbons that can be recovered before the bottoms product is classed as a residuum or residue.

Most often the crude oil fractionation unit is a very large, complex column that separates the crude oil into multiple components: gas, light naphtha, heavy naphtha, kerosene, gas oil, and residue, and not just a topping operation.

Tower fractionation

A fractionation tower is a distillation column, typically with multiple trays or fractionation stages and with at least one feed and two product streams—top and bottom—but often having also provision for multiple feeds and multiple withdrawal points or side cuts.

The mechanical design of a fractionation tower is far more complex than just the specification of the operating conditions or the number of theoretical stages. Also needed will be the specification and design of its components, such as dimensions, plates or packing, risers, downcomers, internal supports, distributor nozzles, reboilers, condensers, etc.

The fractionation trays are normally divided into a minimum of three sections: one side is reserved for the reception of the liquid that descends from the plate immediately above, the middle part is reserved for liquid/vapor contacting, and the other side is reserved for the overflow of the liquid that will flow to the plate immediately below. These sections can vary in number and shape according to various criteria. Thus, for example, large columns may consist of multiple passes with downcomers and overflows arranged at various positions across the plates. The liquid may flow across the plate in the diagonal direction, or it may reversed by using suitable barriers, or it may flow radially. The downcomers and also the overflows may be straight along a chord of the cylindrical vessel or may consist of circular pipes, among other possibilities. The liquid overflow may flow over straight, curved, or cylindrical weirs. In exceptionally large columns, the trays may be stepped internally in tiers, with the liquid flowing over weirs from step to step. The intent is always to provide as much liquid/vapor contacting while avoiding the bypass of liquid across the plate or of vapor through the liquid.

One of the oldest types of contactors is the bubble-cap tray (Figure 19.T.2) in which the ascending vapors are introduced into the descending liquid through a number of slots or serrations cut along the periphery of cylindrical caps screwed onto the top of the plates and usually arranged according to a triangular pitch. Bubble-cap trays are fairly flexible, but are also fairly expensive to fabricate and install. Other types of trays have been used. The simplest and possibly also the most common are sieve trays, that consist simply of a stack of perforated plates, always with provisions for downcomers and overflows (Figure 19.T.3).

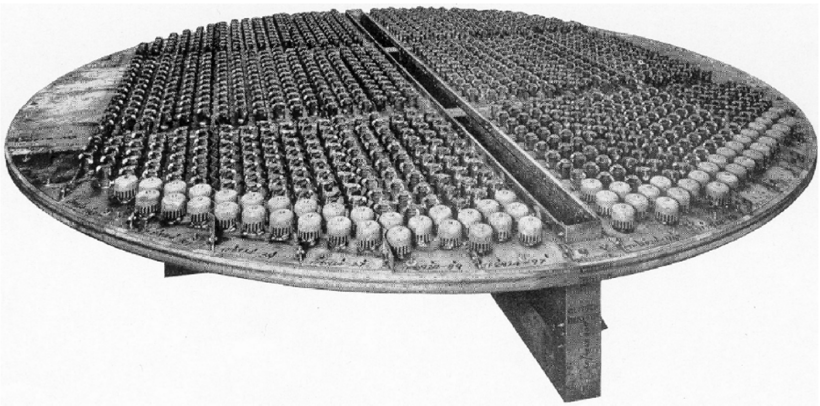


Figure 19.T.2. Conventional bubble-cap tray.

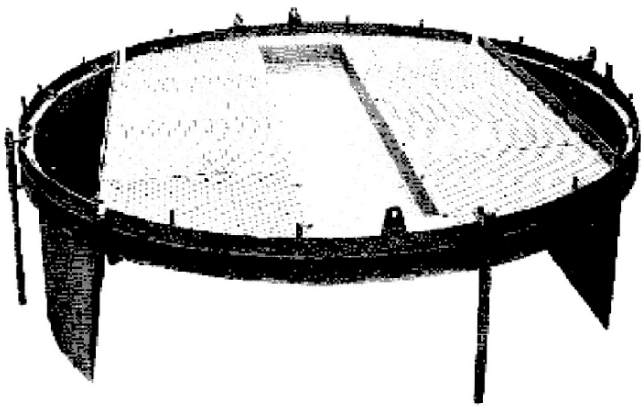


Figure 19.T.3. Conventional sieve tray.

The perforations may be in the form of round holes drilled in the plate, usually with a triangular pitch, or in the form of perforated slots cut or stamped into the trays using a variety of methods (Kittel plates, Turbogrid trays, etc.). Sieve trays are relatively inexpensive and are also fairly flexible but have more load limitations than bubble caps, both in terms of liquid weeping at low vapor loads or of vapor spouting in the case of low liquid loads. A suitable compromise is sometimes the use of valve trays in which metal valves, usually circular or rectangular, are allowed to ascend or descend within the liquid depending on the pressure differential exerted by the ascending vapors.

All these trays offer considerable mechanical complexity and are prone to fouling when used in "dirty" service. Other plates like disk-and-doughnut plates, slanted

cascading plates, etc. can be used for dirty service since they may be more tolerant to fouling, avoid the accumulation of foulants, or may be easier to clean, but these types of plates usually have much lower contacting efficiencies than the traditional types.

It should evident that the correct operation of a fractionation column requires a delicate equilibrium among all the flows and the pressure gradients across the trays. If, for example, the liquid capacity of the column is increased, the quantity of liquid on the trays and in the downspouts will also increase, and so will the pressure differential across the plate. This may cause even more liquid to back up the downspouts and the system becomes unstable. The outcome usually is that the column fills up with liquid or, in common terms, it becomes *flooded*. It is, therefore, important to design the column for operation at a point sufficiently distant from *flooding*—usually about 70% or 80%—that this situation will not arise. *Flooding* can be related to a number of parameters: flow rate of the liquid or vapor is but one of them; another could be the separation between plates that affects the static pressure head, and also the frothing characteristics, if any, of the liquid. It is usually recommended to maintain a tray spacing equal at least to twice the height of the liquid in the downspout, but these rules are often violated in order to save in column height and cost. Other solutions that allow for the reduction of the spacing between trays may include the use of multiple downcomer trays, often denoted as MD trays (Figure 19.T.4).

MD trays may have different layouts with various downcomer arrangements available that can vary from parallel to cross flows at 90° angles. In the latter case, the trays have two-fold symmetry around two centerlines, which intersect at 90°. This symmetry arises from the rotation by 90° of the inlet downcomers with respect to the outlet downcomers on the next tray. This rotation also forces the liquid to flow across the tray in a 90° turn. MD trays allow for relatively short tray-to-tray distances. Several diameters up to 12–15 m have been commercialized. Multiple upcomer (MU) trays also exist and are often used in liquid–liquid extraction applications.

In all of the above the separations are effected by contacting the liquid and the vapor across mechanical (usually metallic) discrete units (trays or plates). Another possibility is to contact descending liquid with ascending vapor over an extended surface like that provided by the presence of a coarse or porous packing within the distillation vessel. Such packings usually have uniform metallic, ceramic, or polymeric structures like Raschig rings, or Berl saddles, or may even consist of rigid interlaced packing structures (usually metallic but sometimes also ceramic). The number of stages in this case is not discrete as in a tray column but, instead, is calculated on the basis of the *height equivalent of a theoretical plate* (HETP) or the *height of a transfer unit* (HTU). These columns usually have no upcomers or downcomers or other mechanical dividers (except for provisions to hold the packing in discrete segments for mechanical

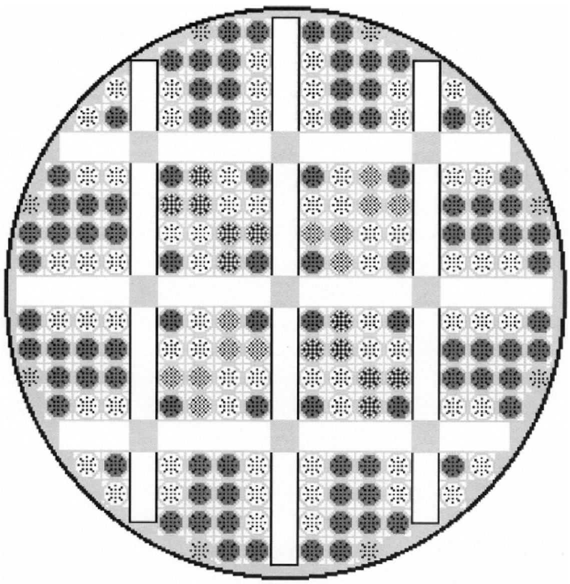


Figure 19.T.4. Typical layout of an MD tray.

purposes). Flooding is also a limitation that the designers have to contend with in packed columns (see also Chapter 18).

True boiling point (TBP)

The true boiling point distillation curve is obtained in a laboratory apparatus that is insulated from the surroundings. The outer jacket is maintained at substantially the same temperature as the temperature of the vapor within the column so that no heat is gained or lost across the fractionation stages and the column is as close to adiabatic as possible. This is often done by circulating heated air through the jacket but it can also be approached by carefully controlled zone heating. Depending on the material being distilled, true boiling point distillation may require operation under vacuum, so the apparatus is usually designed to accommodate such situations.

Distillation may be conducted either at a constant or at a variable rate. If operated at a constant rate, a smooth curve is obtained that reflects the variation in the still temperature as a function of the percentage distilled overhead. In the variable rate method the rate of distillation is adjusted depending on the amount of material that boils at each temperature. In all cases, sufficient reflux should be provided to keep

the packing wet and at the maximum rate that the column will tolerate without flooding.

TBP distillation differs from an ASTM or *Engler* distillation in a number of ways. In an ASTM distillation, the hydrocarbons are distilled at a uniform rate of about 5 cc per min. The distillate is condensed and the temperature of the vapor when the first drop of condensate drips from the condenser is recorded as the Initial Boiling Point (IBP). The vapor temperature is then recorded at each successive 10% interval. When 95% had distilled the temperature of the still may have to be increased and the maximum temperature is recorded as the end point (EP). There is virtually no fractionation in an ASTM distillation. The hydrocarbons do not distill one by one according to their boiling points but only as successively higher and higher boiling mixtures.

Various correlations exist to relate TBP, ASTM, and other laboratory distillation procedures (1) (See also Chapter 1 and Chapter 3).

1. Nelson, W. L. *Petroleum Refining Engineering*, McGraw-Hill, 4th edition, 1958.

UOP K

The *UOP K*, or the *Watson K*, or the *Watson characterization factor*, is a parameter identified by Kenneth Watson (1) who defined it as follows:

$$K = [T_B]^{1/3}/(\text{sp.gr.})$$

where $[T_B]^{1/3}$ represents the cube root of the average molal boiling point of the hydrocarbon mixture $[T_B]$ in degrees Rankine ($^\circ R = ^\circ F + 460$), divided by the specific gravity at 60°F, relative to water at 60°F.

This is a correlation parameter based on the observation that $K \sim 12.5$ corresponds to paraffinic materials while $K \sim 10.0$ indicates a highly aromatic material. It provides a means for roughly identifying the nature of a feedstock solely on the basis of two observable physical parameters.

The characterization factor has also been related to viscosity, aniline point, molecular weight, critical temperature, percentage of hydrocarbons, etc. so it can be estimated using a number of laboratory methods (2).

1. Characterization of petroleum fractions, *Ind. Eng. Chem.*, **27**, 1460, 1935.
2. Nelson, W. L., Petroleum Refinery Engineering, McGraw-Hill, 4th edition, 1958.

Urea dewaxing

A process for producing low pour point oils in which straight-chain paraffins are removed from the feedstock by complexing them with urea to form a crystalline adduct that can be separated by filtration.

It is interesting that, in the adducts, urea forms spiral structures connected by hydrogen bonds in a hexagonal crystalline structure with an internal channel diameter of about 5 angstrom into which only molecules with a smaller cross-sectional dimension can fit (1). In a sense, this behavior mimics the separation of n-paraffins from hydrocarbons with 5A molecular sieves that is extensively used in industry either for the production of heavy n-paraffins or, in combination with paraffin isomerization for the enhancement of the octane number of hydrocarbons in the gasoline boiling range. Heavy n-paraffins can be cracked to linear α-olefins or can be catalytically dehydrogenated to linear internal olefins; both are extensively used in the detergent industry as feedstocks for the production of detergent alcohols or of biodegradable linear alkylbenzenes. (See also Chapter 12.)

1. John J. McKetta (ed), *Petroleum Processing Handbook*, Marcel Dekker, 1992.

V

Vacuum distillation unit

Vacuum distillation unit refers to the further distillation of the residue portion of atmospheric distillation of the crude. The boiling curve range of this portion of the crude is too high to permit further vaporization at atmospheric pressure. Cracking of the residue would occur long before any temperature level for effective distillation would be reached. By reducing the pressure, however, the danger of cracking in further heating the residue oil for further distillation is reduced. Figure 19.V.1 is a process diagram of a typical crude oil vacuum distillation unit. These units operate at overhead pressures as low as 10 mmHg. Under these conditions, the hot residue feed from the atmospheric distillation unit is partially vaporized in a fired heater and enters the vacuum distillation tower at temperatures around 700°F. The hot vapors rise up the tower to be successively condensed by a cooled internal reflux stream moving down the tower as was the case in the atmospheric distillation unit. The condensed distillate streams are taken off as side stream distillates. There is no overhead distillate stream in this case. The high vacuum condition met with in these units is produced by a series of steam ejectors attached to the unit overhead system.

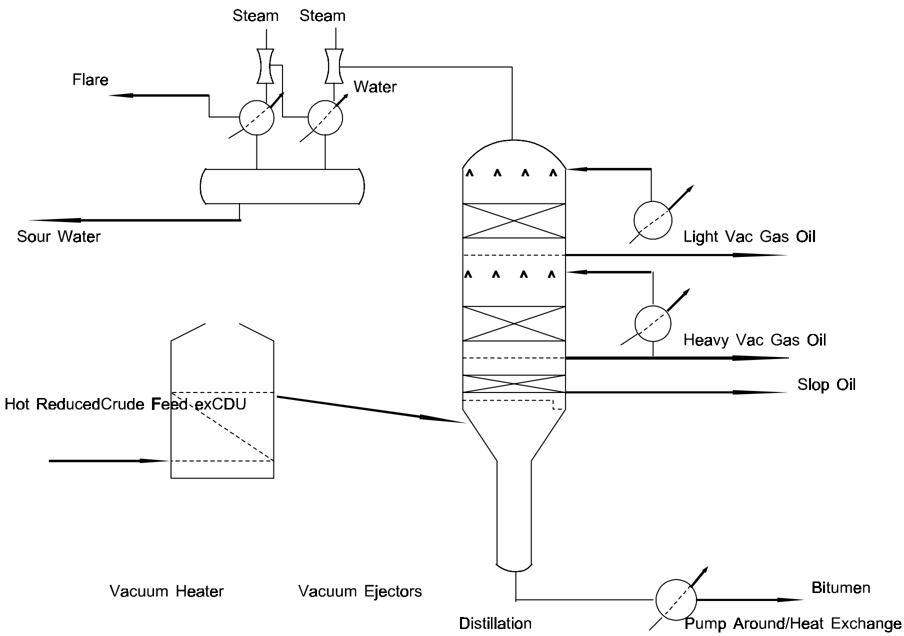


Figure 19.V.1. Vacuum distillation

A low-pressure drop within the tower allows for a flash zone pressure sufficiently low to accommodate the flash temperature of the feed below its cracking temperature (i.e., around the 700–750°F). Typical side stream products from this unit are as follows:

Top side stream	Light vacuum gas oil	690–750°F cut point
2nd side stream	Heavy vacuum gas oil	750–985°F cut point
Residue	Bitumen	+985°F cut point

The low-pressure drop tower internals are beds of proprietary grid packing. A portion of the respective side stream draw off is routed through coolers to be returned as a cool pumparound reflux stream to the packing section above each draw off tray. This unit is further described and discussed in Chapter 3.

Visbreaking process

The visbreaking process is a mild thermal cracking of crude oil residues. It is used to reduce the viscosity of vacuum residue to meet the fuel oil specification. The process configuration is very similar to the conventional once through thermal cracker except

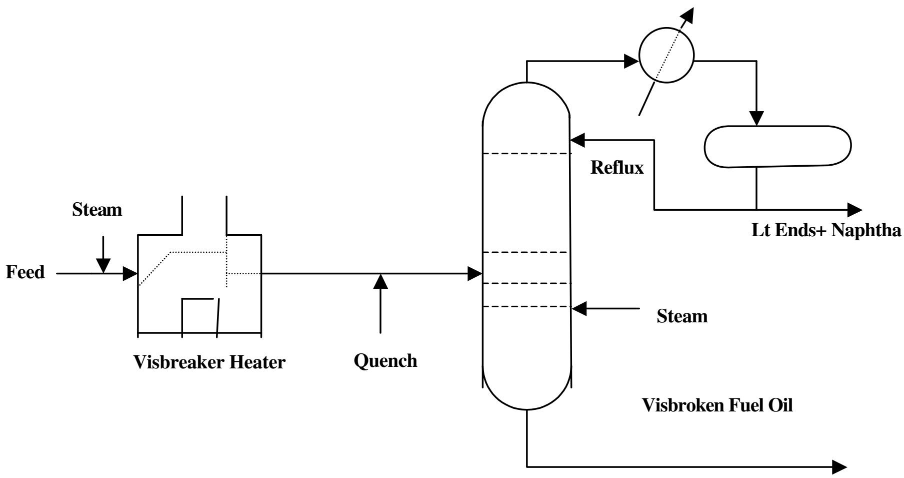


Figure 19.V.2. Typical visbreaker unit.

for the routing of the recovery products from the fractionator. Figure 19.V.2 shows the configuration of a typical visbreaker.

The cabin type heater has two sections: a heating section and a soaking section. A fire wall separates the two sections, a configuration similar to any thermal cracker. The residue feed enters the heater section together with high-pressure steam and is heated to a temperature of around 780–800°F before crossing over the separating fire wall to the soaking section. Here it is allowed to remain for a calculated period of time at a temperature slightly higher than the temperature it reached in the heater section. Some mild cracking occurs so as to produce some range of lower boiling material. The heater effluent leaves the heater to be quenched with cold fuel oil product before entering the fractionator. Unlike a thermal cracker, only the naphtha and lighter cracked distillate is taken off as an overhead product. There will be no middle distillate cut in this case. That material which has been formed by the cracking mechanism will remain in the visbroken bottom product as fuel oil. The design of the fired heater is the same as for any thermal cracker. Section of Chapter 11, describes 'The Soaking Volume Factor' concept.

Viscosity

The viscosity of any petroleum product is a measure of its resistance to flow. This measurement is important in many facets of process design and indeed is an essential quality of many finished products.

Chapter 16 describes the test method for kinematic viscosity. There are two basic viscosity parameters. They are:

Dynamic or absolute viscosity
Kinematic viscosity

Both are related since the kinematic viscosity may be obtained by dividing the dynamic viscosity by the mass density. The metric unit for viscosity is called the *poise* (P). The unit most often used in the petroleum industry for this measure is the *centipoise* (cP) which is the poise divided by 100. This dimensions of the poise are:

$$\frac{\text{gram}}{\text{cm} \times \text{sec}}.$$

The kinematic viscosity dimension in English units is the *square foot per second*. And in metric units is *square centimeter per second* called *the stoke.* In the petroleum refining industry, the stoke divided by 100, called *the centistoke*, is the unit most often used. When the terms centipoise and centistokes are used the mass density is numerically equal to the specific gravity.

Various types of instruments are available to determine viscosity in other terms. These terms are SSU which is Saybolt Seconds Universal and SSF which is Seconds Saybolt Furol. All viscosity terms can be converted by factors to one another. These factors may be found in most engineering data books such as Cameron Hydraulic Data and The GPSA (Gas Processors Suppliers Association) Engineering Hand Book. Viscosity is used extensively in product blending and quality control of petroleum products. In blending for viscosity, a blending index concept must be used. That is, one cannot blend directly using just volumetric proportions. The viscosity indices are given and discussed in Chapter 1 and again in Chapter 2.

W

Waste disposal facilities

All process plants including oil refineries produce large quantities of toxic and/or flammable materials during periods of plant upset or emergencies. Properly designed flare and slop handling systems are therefore essential to the plant operation. This section describes and discusses typical disposal systems currently in use in the oil refining industry where the hydrocarbon is immiscible with water. Where the chemical is miscible in water special separation systems must be used.

Figure 13.17 in Chapter 13 shows a completely integrated waste disposal system for the light end section of an oil refinery. Further description and discussion of these disposal systems is given in the following sections of that chapter:

- Blow-down and slop disposal
- Flares
- Water effluent treating

Blow-down and slop

This system generally consists of the following drums:

- Non condensable blow-down drum
- Condensable blow-down drum
- Water disengaging drum

Particular emphasis is put on the level control of liquid in these drums.

The flare

Vapors collected in a closed safety system are disposed of by burning at a safe location. The facilities used for burning are called flares. The most common flares used in industry today are:

- The elevated flare
- The multi jet ground flare

The elevated flare is used where some degree of smoke abatement is required. The flare itself operates from the top of a stack usually in excess of 150 ft high. Steam is injected into the gas stream to be burnt to complete combustion and thereby reduce the smoke emission.

The multi jet ground flare is selected where luminosity is a problem. For example at locations near housing sites. In this type of flare, the vapors are burned within the flare stack thus considerably reducing the luminosity. Steam is again used in this type of flare to reduce the smoke emission.

Effluent water treating facilities

This section of the offsite systems deals with the treating of waste water accumulated in a chemical process complex before it leaves the complex. Over the years, requirements for safeguarding the environment have demanded close control on the quality of effluents discharged from chemical and oil refining plants. This includes effluents that contain contaminants that can affect the quality of the atmosphere and those that can be injurious to plant and other life in river waters and the surrounding seas. Effluent

management in the oil industry has therefore acquired a position of importance and responsibility to meet these environmental control demands.

Water effluents that are discharged from the process and other units are collected for treating and removal or conversion of the injurious contaminants. In most oil refineries imported water in the form of ship ballast water is also collected on shore for treatment before discharging back to the sea. Figure 13.26 is a schematic of the water effluent treating system for a major European oil refinery. More details and discussion on waste water disposal are given in Chapter 14.

Water systems

The major water systems generated in most chemical plants are:

- Cooling water
- Treated water for boiler feed water (BFW)

Potable water as raw water is usually drawn from municipal supply. Where water is required for cleaning or drinking this potable water is used without further processing.

Cooling water

The cooling water system is a circulating one. There is a cold supply line with an associated warmer return line. Chapter 13 describes and discusses a typical refinery cooling water supply and return. Figure 13.31 in that chapter shows such a system in some detail.

The water returned to the cooling tower by the return header enters the top of the cooling tower and flows down across the tower internals counter current to an air flow, either induced or forced by fans passing up through the tower. The water cooled by the air flow is collected in the cooling tower basin. Make up water (usually potable water) is added to the basin under level control. Vertical cooling water circulating water pumps take suction from the cooling tower basin sump to deliver the water into the distribution header. The supply header pressure is kept at around 30 psig and, very often in large plants covering long distances, booster stations are installed at predetermined locations to maintain the supply header pressure. The return flow is collected from each user into the return header and flows back to the cooling tower.

Boiler feed water treating

All water contains impurities no matter from what source the water comes from. Appendix 13.2 of Chapter 13, gives a listing of the common impurities found in

water for industrial use. When it comes to generating steam and particularly high-pressure steam, these impurities become problematic. Appendix 13.2 also provides a description of the effect of these impurities on steam generators and gives the normal means of treating. In general there are three types of soluble impurities naturally present in water and which must be removed or converted in order to make the water suitable for boiler feed. These are:

- Scale forming impurities
- Compounds that cause foaming
- Dissolved gases

Solid build up in the boiler itself is removed or kept at a low level by blow down. Figure 13.32 of Chapter 13 gives an example of boiler blow down.

There are two types of external boiler feed water treatment in common use in the petroleum refining industry. These are.

- The "hot lime" process

This is a water softening process which uses a hot lime contact to induce a precipitate of the compounds contributing to the hardness.

- The ion exchange processes

As the name implies, this process exchanges undesirable ions contained in the raw water with more desirable ones that produce acceptable BFW. The ion exchange material needs to be regenerated after a period of operation. The operating period will differ from process to process and will depend to some extent on the amount of impurities in the water and the required purity of the treated water. Regeneration is accomplished in three steps:

- Back washing
- Regenerating the resin bed with regenerating chemicals
- Rinsing

These two systems are described in detail in Chapter 4.

X, Y, Z

Xylenes

These are aromatic compounds which are coupled with benzene, toluene, and ethyl benzene as the major products from a petrochemical petroleum refinery. These compounds as a whole are usually designated as BTX. The process begins in a conventional

refinery with the catalytic reforming of a high naphthene content naphtha. This naphtha may be the product of a hydrocracker. The reformate is much richer in aromatics than that used for gasoline production. After stabilizing, the reformate enters an extraction unit where residual paraffins are removed, and the rich aromatic stream is routed to an aromatic splitter. Depending on the severity of the reformes the splitter may be located ahead of the extraction unit since the xylenes may not require extraction. The benzene and toluene components are taken off as overhead distillate and the bottom product enters a super fractionation unit, the xylene splitter. Here ethyl benzene, para-xylene, and meta-xylene are taken off as overhead distillates. Para-xylene may be separated from this overhead distillate by absorption or crystallization, or may continue with the remaining distillate to enter an isomerization unit, where they are isomerized into a rich ortho-xylene stream. Para-xylene product is by far the more valuable and important isomer of the C_8 aromatics.

Ortho-xylene stream leaves as the bottom product of the isomerizer splitter tower to be returned to the xylene splitter super fractionator tower. The bottom product of this tower is the ortho xylene product. Further details and description is given in Chapter 12. Figure 18 of this chapter, shows a process configuration of a typical BTX process. Ortho-xylene is used extensively in the production of phthalates, para-xylene is used in the production of terephtualic acid and polyesters, and ethylbenzene is used in the production of styrene.

'Z' Factor

"Z" is often the symbol used for the compressibility factor of a gas. This may be derived from the equation:

$$PV = ZnRT$$

$$PV = Z\frac{m}{M}RT$$

$$PM = Z\rho RT$$

$$Z = \frac{PM}{\rho RT}$$

Where:

V = volume of gas, m = mass of gas, R = gas constant
M = mole weight of the gas
P = gas pressure (absolute)
T = absolute temperature
ρ = density of the gas at gas temperature and pressure

Typical values for R are:
8.3143 J/(mol · °K)
0.08205341 atm · m^3/(kmol · °K)
1.98716759 cal/(mol · °K)
10.7313 psia · ft^3/(lb mol · °K)

Zeolite catalysts

Zeolite catalysts are used in catalytic cracking processes. This together with the technique of 'Riser Cracking' revolutionized these processes (distillate feed crackers and residuum feed). This is described and discussed in detail in Chapter 6.